

Experimental Investigation on The Synthesis of Copper Nanoparticles By Chemical Reduction Method

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Abstract-Highly stable dispersion of nanosized copper particles was prepared by chemical reduction method. Chemical reduction of copper salts by L-ascorbic acid is a new and green approach in which L-ascorbic acid is used as reducing and capping agent in aqueous medium. This approach is the most effective and is also economical. The effects of reactant concentration and reaction temperature on morphology of dispersed copper nanoparticles were studied. The formation of copper nanoparticles in dispersion was monitored through the analysis of absorbance spectra by UV-Visible Spectrophotometer at different stages during the process of synthesis. The morphology of copper nanoparticles was characterized by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The product of adding L-ascorbic acid in copper salt was characterized by Fourier Transform Infrared (FTIR) Spectrophotometer. The study revealed that L-ascorbic acid plays an important role of protecting the copper nanoparticles to prevent oxidation and agglomeration and they have good stability for application.

Index Terms: Copper nanoparticles, Experimental Conditions, L-Ascorbic acid, Oxidation resistance, Chemical reduction.

1 INTRODUCTION

Nanotechnology is the most promising technology that can be applied almost all sphere of life, ranging from electronics, pharmaceuticals, defense, transportations heat transfer to sports and aesthetics. Metallic nanoparticles are of great interest due to their excellent physical and chemical properties such as high surface to volume ratio and high thermal conductivity. Amongst them copper nanoparticles are paid more attention due to their low cost and easy availability. Copper nanoparticles have also been considered [1], [2] as an alternative for noble metals in many applications such as heat transfer and micro electronics [3]. The micro fabrication of conductive features like inkjet technology is common. So for electronics devices have utilized noble metal like gold and silver for printing highly conductive element while cost of noble metals are very high, copper is low cost, conductive material, therefore it is economically attractive.

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Copper nanoparticles have been synthesized by different methods such as thermal reduction [4], thermal decomposition [5], [6], electrochemical reduction [7], mechano-chemical process [8], chemical reduction [7], [8], [9], [10], [11] have all been developed to prepare copper nanoparticles. Chemical reduction method is one of the most convenient methods for the synthesis of metallic nanoparticles because this synthesis process is simple, shape and size of nanoparticles can be controlled. The main question arises from the stability of copper nanoparticles including the extremely sensitive to oxygen and colloidal agglomeration. Therefore there are several approaches related to the dispersion and oxidation resistance that needs to be solved before application. Some study reveals that to protect copper nanoparticles against oxidation during preparation and storage, ascorbic acid is utilized as reductant and antioxidant of nanostructured Copper [12].

Despite that oxidation resistance and dispersion are of immense importance in several applications but few studies have been carried out in this area. So in the present study, the influence of L-ascorbic acid, different concentration of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and reaction temperature on the oxidation and dispersion of the aqueous copper nanoparticles were investigated. Copper nanoparticles were prepared with single reduction method without protective gas and synthesis was studied by UV-Visible Spectrophotometer, SEM and TEM and FTIR Spectrophotometer.

2 EXPERIMENTAL

2.1 Material

For the present work, we used analytical grade chemicals such as copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ -97%) and

L-ascorbic acid (vitamin C-98%) purchased from E. Merck. All chemicals were used as received without further purification. Double distilled water was employed throughout the study.

2.2 Synthesis of Copper Nanoparticles

In a synthetic procedure, copper nanoparticles were obtained via a wet chemical reduction route. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ aqueous solution was prepared by dissolving $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.02M) in 50 ml deionized water. The flask containing aqueous solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was heated to 80°C in oil bath with magnetic stirring. 50 ml of L-ascorbic acid aqueous solution (0.1M) was added drop wise into the flask while stirring. With the passage of time, the color of dispersion gradually changed from white, yellow, orange, brown finally dark brown with a number of intermediate stages. The appearance of yellow color followed by orange color indicated the formation of fine nanoscale copper particles from L-ascorbic acid assisted reduction. The resulting dispersion was centrifuged for 15 minutes. The supernatant was placed under ambient conditions for 2 months. Various optimization studies were performed to investigate the size and shapes of copper nanoparticles.

2.3 Characterization

UV-Visible spectroscopy from a double beam spectrophotometer (U.V. 3000+ LABINDIA, path length 1.0cm spectral range from 200 nm to 800 nm) was used for preliminary estimation of copper nanoparticles synthesis. FTIR (ALPHA-T -Bruker) provided information about the binding interactions of L-ascorbic acid with zero valent copper particles. Morphological study of the copper nanoparticles was carried out with scanning electron microscopy (SEM) (EVO 18 carlzeiss) image analysis, for which dispersed nanoparticles were centrifuged and ultrasonicated for 40 minutes. 30 μl aliquots were then extracted and deposited on stub for SEM analysis. Transmission electron microscope (TEM) (FEI Techni G2S2 Twin) images were recorded to confirm size distribution and shape homogeneity of newly synthesized copper nanoparticles. Samples were prepared by taking small quantities of copper nanoparticles separated by centrifugation then ultrasonicated dispersed suspensions were mounted on carbon coated copper grids.

3 RESULTS AND DISCUSSION

3.1 Effect of L-ascorbic acid as reducing agent

UV-Visible absorbance spectroscopy has proved to be a very useful technique for studying metal nanoparticles because the peak position and shapes are sensitive to particle size. The syntheses of copper nanoparticles were

recorded by UV-Visible spectra at every color change (Fig. 1.)

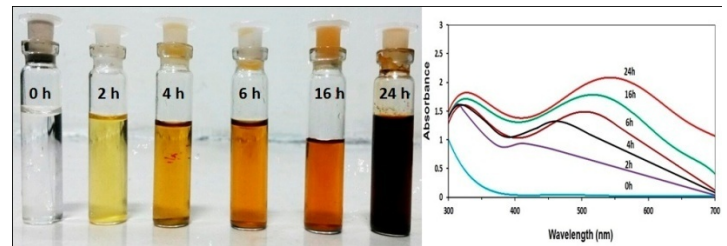


Fig.1. The time evolution of the dispersion photographs and the UV-Visible absorption spectra

The effect of L-ascorbic acid concentration (0.08M, 0.09M, and 0.1M) on the UV-Visible absorbance spectroscopy of the synthesized copper nanoparticles is shown in Fig. 2.

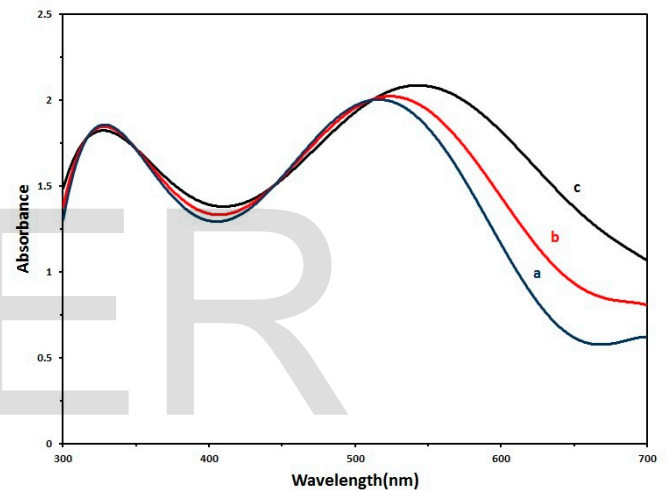


Fig.2. The UV-Visible absorption spectra of copper nanoparticles stabilized in L-ascorbic acid with various concentrations: (a) 0.08M, (b) 0.09M, (c) 0.10M

The first absorption peak of different curves is at 335 nm corresponding to oxidation product of L-ascorbic acid [13]. The second absorption peak is increasingly broadening with an increasing concentration of L-ascorbic acid. The absorption peak of copper nanoparticles has been reported at around 560 nm of UV-Visible wavelength which proves the formation of copper nanoparticles [14], [15]. In this work, the resulting copper nanoparticles did not show a peak at 560 nm but displayed a broadened peak at short wavelength, indicating the presence of small separated copper nanoparticles.

TEM images of the synthesized copper nanoparticles are shown in Fig. 3. at different concentration of L-ascorbic acid.

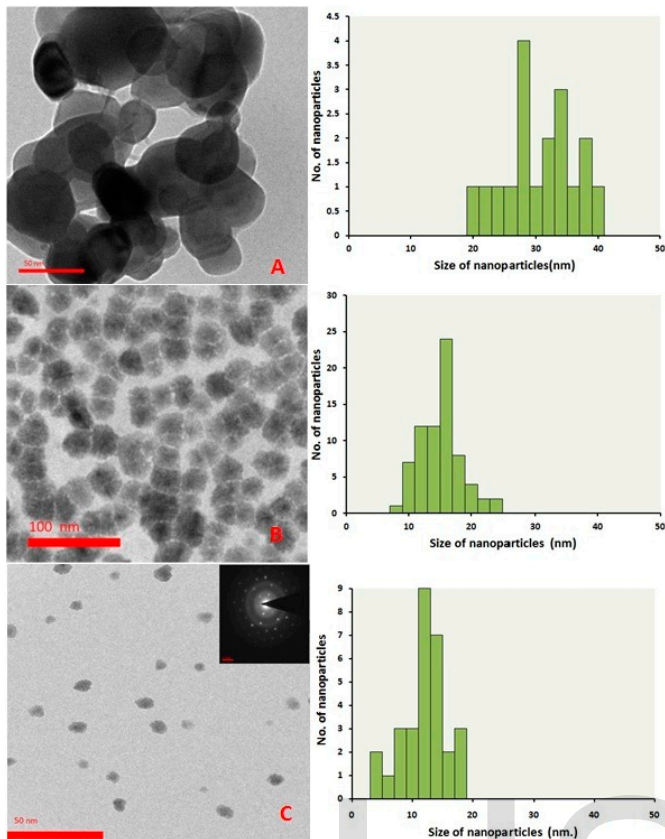


Fig.3. TEM images with histogram of copper nanoparticles with variable concentration of L-ascorbic acid ((A) 0.08M, (B) 0.09M, (C) 0.1M)

The histograms of copper nanoparticles size distribution are also presented in Fig. 3. The particles are spherical in shape. The histogram reveals a decrease in particle size with increase of L-ascorbic acid concentration. The size of the copper nanoparticles with various concentration of L-ascorbic acid are (0.08M, 0.09M, 0.10M) 28nm, 16nm, 12nm respectively. The reason is that the number of Cu^{+2} encapsulated in ascorbic acid molecules decreases with increasing concentration of L-ascorbic acid, leading to the formation of small copper nanoparticles.

3.2 The effect of initial concentration of precursor salt

There are two stages when copper nanoparticles generate in the solution. The first stage is to generate copper nuclei and second stage is the growth of copper [16]. So it is important to control preparation process that copper nuclei must generate faster and grow up slower which requires better control of the initial concentration of Cu^{+2} . In this experiment the concentration of precursor salt is varied from (0.01M to 0.03M). It can be seen that reaction rate increases with increases the concentration of Cu^{+2} . With the increasing reaction rate, the amount of copper nuclei rises and smaller particle size are obtained correspondingly. The SEM images of the synthesized copper nanoparticles are shown in Fig. 4. The SEM results indicate that an excess

number of nuclei will be generated when the reactant concentration is too high. This result is the agglomeration of the nuclei and growing the particles size. This may be due to collision between small particles, which leads to particle growth [17]. So the optimal concentration of precursor salt is 0.02M.

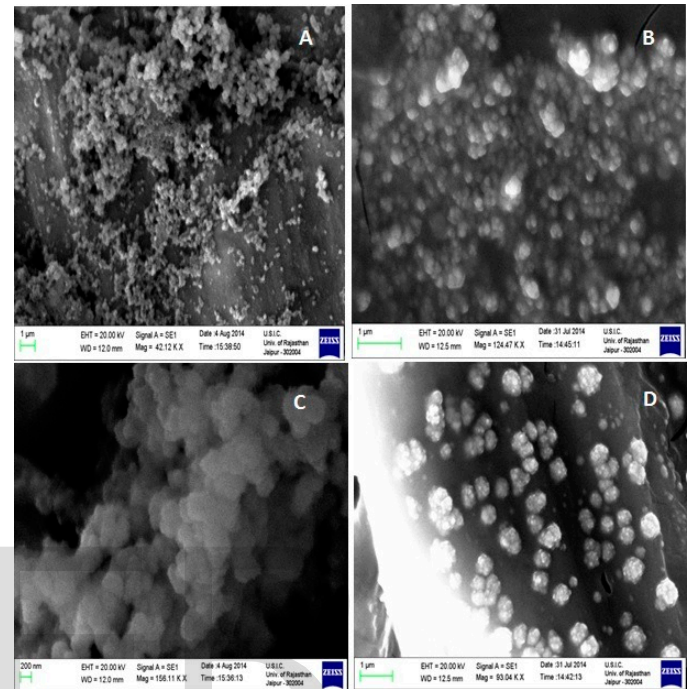


Fig. 4. SEM images of the synthesized copper nanoparticles with various concentration of the precursor salt ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (A) 0.01M, (B) 0.015M, (C) 0.02M, (D) 0.03M

3.3 Effect of reaction temperature

The present investigation reveals that nanoparticles did not form below the temperature 60°C in any conditions. Therefore reaction temperature higher than 60°C with appropriate concentration of the reactants should be inserted to the synthesis of copper nanoparticles.

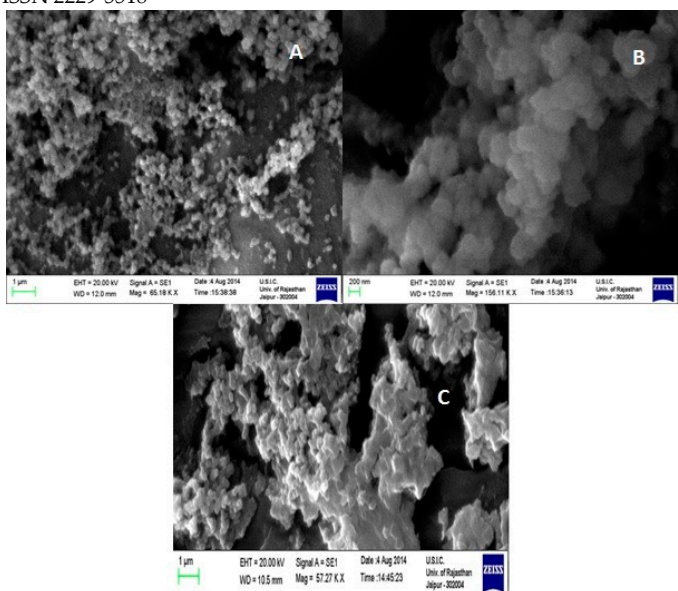


Fig.5. SEM images of synthesized copper nanoparticles with variation of temperature 70°C to 90°C (A) 70°C, (B) 80°C, (C) 90°C

In Fig. 5. SEM images of copper nanoparticles synthesized at 70°C, 80°C, 90°C respectively, shown that at higher temperature (90°C), the nanoparticles were agglomerated, while at 80°C are well dispersed with an average size at about 12 nm. Basically, the reduction of Cu^{+2} were increase by increasing the reaction temperature. Therefore the synthesis rate is too high to control particle size at high temperature. When reducing agent adds to precursor solution at 90°C, rate of growth and agglomeration as well as nucleation of copper nanoparticles accelerated almost coincidentally. These phenomena result in the formation of copper nanoparticles were precipitated. Therefore moderate temperature (80°C) should be selected for synthesis of the copper nanoparticles with appropriate controlling on size.

3.4 The stability of copper nanoparticles

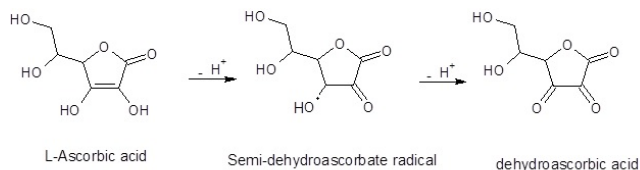
The stability of nanoparticles dispersion is key factor in their application. In this study L-ascorbic acid was used as both reducing and capping agent without any other special capping agent. The photographs of dispersion before and after the storage (2 months) are shown in Fig. 6.



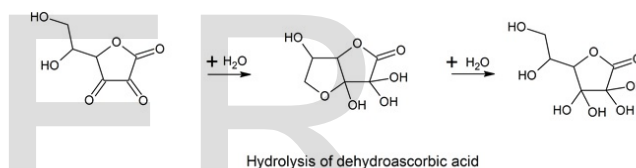
(A) (B)

Fig.6. The photos of dispersion of copper nanoparticles (A) before and (B) after 2 months of storage

During the synthesis process, excessive L-ascorbic acid is essential to avoid the oxidation of copper nanoparticles. The antioxidant properties of L-ascorbic acid come from its ability to scavenge free radicals and reactive oxygen molecules [18], accompanying the donation of electrons to give semi-dehydroascorbate radical and dehydroascorbic acid.



The dehydroascorbic acid has three carbonyl in its structure. The 1, 2, 3 tricarbonyl is too electrophilic to survive more than a few seconds in aqueous solution. Hydration of 2-carbonyl is also reported [19]. Finally the polyhydroxyl structure is obtained through hydrolysis [13].



The excessive number of hydroxyl group can be facilitated the complexation of copper nanoparticles to the number of matrix by inter-intramolecular hydrogen bond and thus prevent the agglomeration of copper nanoparticles. The result is confirmed with FT-IR Spectrophotometer (Fig. 7.).

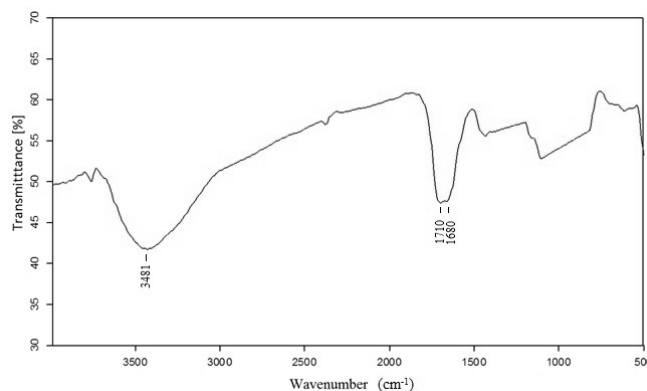


Fig.7. FTIR spectra of L-ascorbic acid stabilized copper nanoparticles

FTIR spectrum shows the peaks at 3481 cm^{-1} , 1710 cm^{-1} and 1680 cm^{-1} . These peaks corresponds to the hydroxyl, oxidated carbonyl group and conjugated carbonyl group

respectively. These results indicate the presence of polyhydroxyl structure on the surface of copper nanoparticles. Therefore L-ascorbic acid plays dual role as reducing agent and antioxidant of copper nanoparticles. Thus reaction can complete without any protective gas.

4 CONCLUSIONS

The study suggests that synthesis route is low cost, environmental friendly and can be prepared in simple laboratory equipment in ambient condition. By this method synthesized monodispersed copper nanoparticles (ranging from 12nm to 28nm) by employing different concentration of L-ascorbic acid as both reducing and capping agent. The prepared copper nanoparticles are highly stable and do not show sedimentation even after storage for 2 months. Moreover, it was clearly shown that the initial concentration of reactant and reaction temperature has a remarkable effect on particle size and agglomeration of the synthesized copper nanoparticles.

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