Experimental Investigation on the Synthesis and Size Control of Copper Nanoparticle via Chemical Reduction Method

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Abstract:
In this study, synthesis of copper nanoparticles and effect of the reaction conditions on the particle size were investigated. The copper nanoparticles were synthesized and stabilized in a narrow temperature range in the presence of polyvinylpyrrolidone under nitrogen atmosphere. Reaction temperature and concentration ratio of the reducing agent to the precursor (R/P) as two main conditions influenced the reaction progress and size on the copper nanoparticles. This study showedn that the copper nanoparticles were formed when parameter R/P was greater than 2 (4 and 6) in the temperatures ranges of 60 to 75°C. The averaged size of the synthesized copper nanoparticles in the optimized conditions was about 30 nm. The rResults showed that the synthesized copper nanoparticles were oxidized due to the exposure to air for a long time and thereafter it re-dissolves in the aqueous solution.
Keywords: *Copper nanoparticles, Reaction conditions, Precipitation method, Chemical reduction*

1. INTRODUCTION

Metallic nanoparticles have drowned lots of attention throughout recent decades, because their chemical and physical properties are dependent of size and shape of the powders. For example melting point of metals decreases sharply when their size decreases to nanosize. Among metal nanoparticles, copper nanoparticles have attracted much attention because of their catalytic and optical properties and high electrical and heat conductivity. Copper nanoparticles in comparison with the bulk copper are potentially suitable materials for use in printed electronics and good substitutes for conductive and expensive noble metals like gold and silver [1].

Synthesis of nanostructure copper particles was studied based on the different methods such as chemical reduction in aqueous solutions [1-4], colloidal synthesis with reduction and extraction steps [5], evaporation and condensation of metal vapor on a cold surface [6,7], electrochemical methods [8], sonochemical reduction [9], polyol method in which reduction takes place in alcoholic media at high temperatures [10,11] and hydrothermal process [12].

Synthesis of copper nanoparticles by reduction in aqueous solutions and precipitation the nanoparticles is a laboratory method, which has many parameters affecting on the nucleation, growth and agglomeration phenomena and consequently particle size distribution. The parameters such as temperature, reaction time, reducing agent and

precursor type and concentration, additive type and amount and even mixing affect on the size of copper nanoparticles.

In the present study, synthesis of copper nanoparticles in an aqueous solution was investigated by simple reduction of copper ions with sodium borohydride as reducing agent and polyvinylpyrrolidone as stabilizer. In addition, effects of the reaction parameters on the formation and size control of the copper nanoparticles were studied.

2. MATERIALS AND METHODS

2.1. Materials

The main chemicals used in this study were copper sulfate pentahydrate ($CuSO_4$.$5H_2O$, Merck) as precursor, sodium tetrahydridoborate ($NaBH_4$, Merck) as reducing agent and polyvinylpyrrolidone (PVP, Merck) as stabilizer.

2.2. Method

A solution of 0.001 molar $CuSO_4$ and 5 gr/lit of PVP were prepared by dissolving appropriate amount of the salt and the solid polymer in distilled water. The solution was purged by nitrogen to remove oxygen from atmosphere of the solution. Then the solution was heated and stirred to the reaction temperature in the inert atmosphere (nitrogen gas). Thereafter, 10 ml of $NaBH_4$ solution with a predetermined concentration were added to the solution. Light blue color of the solution changed very quickly to different colors, which ranges from orange to dark red and black according to the reaction conditions. The concentration ratio of reducing agent ($NaBH_4$) to precursor ($CuSO_4$), which is named parameter R/P, and reaction temperature were considered as the most effective synthesis conditions.

The nanosuspension solution was analyzed with a VinCary 50 UV-vis Spectrophotometer for detecting the formation of Cu nanoparticles. Particle size distribution was analyzed by Zeta sizer Nano series of Malvern Instruments. TEM images of the synthesized copper nanoparticles were prepared by a transmission Electron Microscope (CEM 902A, zice Germany, 120 KV). A Scanning Electron Microscope (CAMSCAN, 2600 MV) is used to energy dispersive X-ray spectroscopy (EDS) analysis of the samples.

3. RESULTS AND DISCUSSION

3.1. Reaction conditions for formation of copper nanoparticles

The synthesis of copper nanoparticles was carried out by the chemical reduction of $CuSO_4$ with $NaBH_4$. The reaction conditions and formation of Cu nanoparticles based on the UV-vis Spectroscopy are reported in table 1.

As shown in table 1, the copper nanoparticles were not formed at temperatures below 60°C in a wide range of parameter R/P. The copper nanoparticles were formed at temperature range 60 to 75°C and the solution color became dark red when parameter R/P was higher than 2 (4 and 6). All copper nanoparticles formed in these conditions had a UV-vis spectrum as shown in figure 1. This figure shows the UV-vis spectra

Table 1: *Experiment conditions for synthesis of copper nanoparticles.*

Sample No.	Temperature(°C)	R/P	Cu nanoparticles
1	50	2	Not formed
2	50	8	Not formed
3	60	2	Not formed
4	60	4	Formed (not precipitated)
5	60	6	Formed (not precipitated)
6	75	4	Formed (not precipitated)
7	85	4	Formed (precipitated)

of sample No. 4 in table 1 with an absorbance peak in 570 nm of the UV-vis wavelength, which proves the formation of the copper nanoparticles in the solution [2, 11].

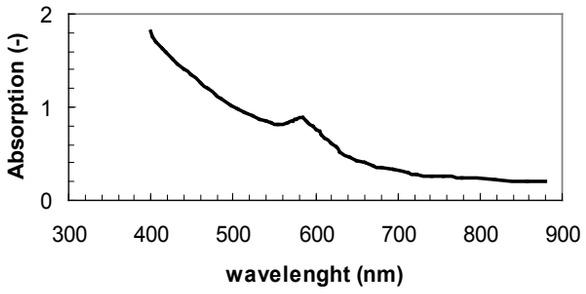

Figure 1: *The UV-vis absorption spectra of synthesized copper nanoparticles.*

When the reducing agent was added to the precursor solution at temperatures higher than 85°C, the solution color became black and then a black precipitate was formed due to acceleration of the reduction rate. The precipitate might be CuO nano and microparticles formed during the process. Thus as a results, formation of copper nanoparticles took place in a narrow temperature range (60-75°C) with the parameter R/P range from 2 to 6.

3.2. The effect of reactants concentration ratio

Figures 2a and 2b show the TEM images of the samples No. 4 and No. 5 in table 1, which were synthesized at temperature 60°C with parameter R/P 4 and 6 respectively. These images were analyzed and the results showed that synthesized nanoparticles had an average size about 30nm for both samples. Figure 3 shows the size distribution of the nanoparticles given by zeta sizer for sample No. 5 in table 1. This analysis clarifies the average size of nanoparticles about 26 nm that is in agreement with TEM image analysis.

The reduction of copper nanoparticles did not take place at temperature 60°C with R/P=2 and therefore nanoparticles were not formed (sample No. 3 in table 1). In this value of parameter R/P, BH_4^- ions are stoichiometrically sufficient to reduce Cu^{2+} ions but BH_4^- may decompose directly to form H_2 [13]. Therefore reduction of Cu^{2+} ions were not complete in R/P=2.

On the other hand for parameter R/P higher than 2 (4 and 6), the reduction rate became independent of the reducing agent concentration. This means that at the high reducing agent concentration in the solution, the precursor concentration has no significant effect on the reduction rate and size of the particles.

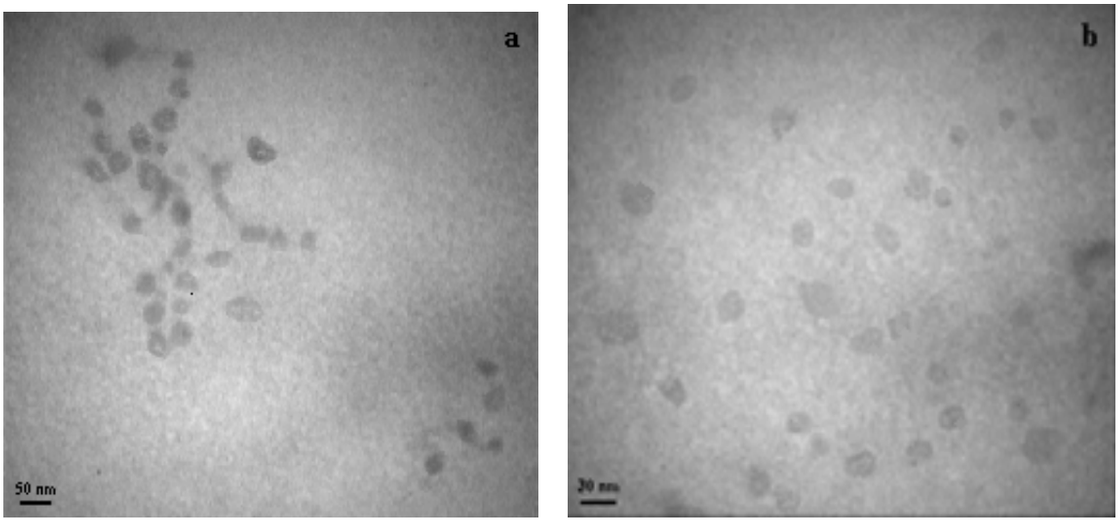

Figure 2: *TEM images of copper nanoparticles synthesized at T=60°C (a) R/P=4 and (b) R/P=6.*

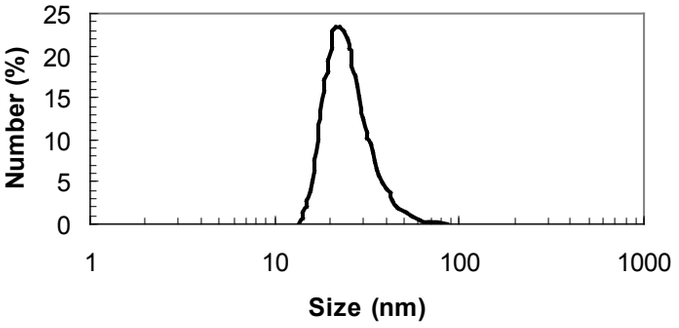

Figure 3: *Size distribution of copper nanoparticle synthesized at T=60°C and R/P=6.*

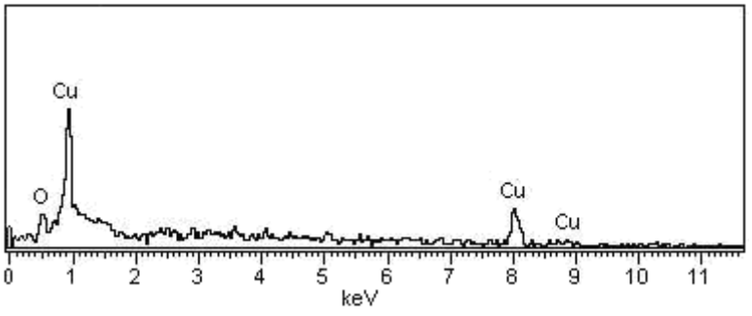

Figure 4: *EDS spectra of copper nanoparticles for sample No 5 in table 1*

Figure 4 shows the Energy Dispersive X-ray Spectra (EDS) of the synthesized copper nanoparticles of the sample No. 5 in table 1. It is clear that the synthesized nanoparticles are copper, which are somewhat oxidized due to contact with air after placing the particles suspension on the grids. The copper nanoparticles were not oxidized during synthesis because whole the reaction was carried out in the inert gas atmosphere and the solutions were purged with the inert gas before the reaction.

3.3. Effect of the temperature

The nanoparticles did not form at temperature 50°C in any reactants concentration. This shows that reaction constant at this temperature is too low to progress the reaction. Therefore, reaction temperature higher than 50°C with appropriate parameter R/P should be inserted to the reaction environment to progress the reaction and synthesis the nanoparticles considerably.

In figure 5, TEM image of the nanoparticles synthesized at T=75°C and R/P=4 (sample No. 6 in table 1) is shown. The image analysis of this TEM image showed an averaged size about 70 nm for the nanoparticles. Figure 6 present the size distribution of the sample with the averaged size of 61.8 nm which is in agreement with the TEM result.

Comparison of this figure with figure 2a shows that the copper nanoparticles synthesized at 75°C have a wider range of size distribution. In addition, the nanoparticles were agglomerated in these conditions while copper nanoparticles synthesized at 60°C are well dispersed with an averaged size about 30 nm.

Basically, the reduction rate of Cu^{2+} ions considerably increases 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 T=85°C, rate of growth and agglomeration as well as nucleation of copper nanoparticles accelerated almost coincidently. These phenomena result in the formation of nanoparticles with higher averaged size of the copper particles were precipitated (sample

No. 7 in table 1). Therefore moderate temperature (60 °C<T<85 °C) should be selected to synthesis of the nanoparticles with appropriate controlling on the size.

3.4. Oxidation behavior of the synthesized copper nanoparticles

To investigate the oxidation resistance of the synthesized copper nanoparticles, the suspension was exposed to the air and then its UV-vis absorption spectra of the suspension was obtained at different times. Figures 7a and 7b show the absorption spectra of the sample No. 4 in table 1 after exposing to air for 5 and 10 minutes, respectively. In these cases the suspension color changed from dark red to light blue. Comparison of these figures with figure 1 (which is the UV-vis spectra of the same suspension without air exposing) shows that the UV-vis spectra peak of copper nanoparticles is removing gradually. The reason is oxidation progressing of the copper nanoparticles that causes re-dissolving and disappearing of the nanoparticles in the solution. Therefore, the stabilized copper nanoparticles by PVP have not a good resistant against oxidation with air for a long time.

4. CONCLUSIONS

In this study, the effect of the reaction conditions on the synthesis of copper nanoparticles was investigated. Results showed that the copper nanoparticles are formed in the temperature ranges of 60 to 75 °C for the concentration ratio of reducing agent to precursor higher than 2 (4 and 6). It was also shown that when the R/P is greater than 4 the reduction rate becomes independent of the reducing agent concentration. In the optimum reaction conditions (i.e R/P=4 at 60 °C), well dispersed copper nanoparticles are formed. By increasing the reaction temperature from 60 to 75 °C agglomerated copper nanoparticles are produced with a wide range of size. Investigation on the oxidation behavior of the copper nanoparticles showed that the synthesized copper nanoparticles have not a good resistant against air.

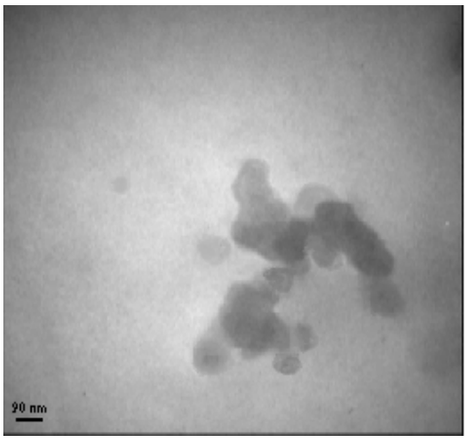

Figure 5: *TEM images of copper nanoparticles synthesized at T=75°C for R/P=4*

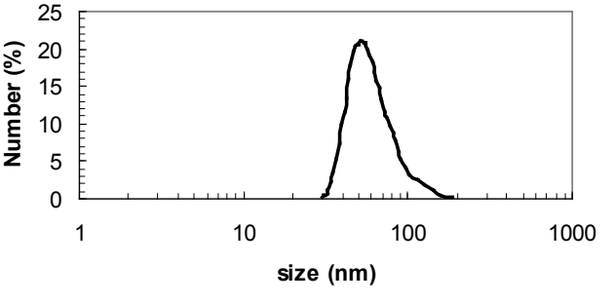

Figure 6: *Size distribution of copper nanoparticle synthesized at T=75°C and R/P=4.*

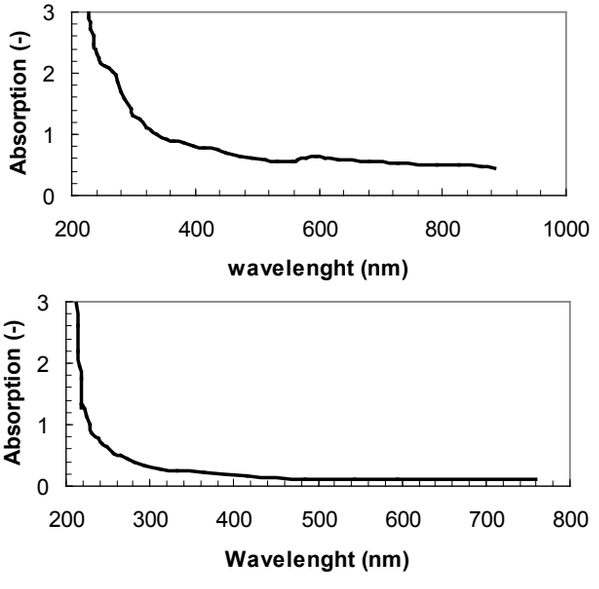

Figure 7: *UV-vis spectra of copper nanoparticles exposed to the air after (a) 5 min and (b) 10 min*

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