

# SYNTHESIS AND CHARACTERIZATION OF METALLIC COPPER NANOPARTICLES AT ROOM TEMPERATURE BY HYDRAZINE REDUCTION METHOD

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## ABSTRACT

In this work, copper nanoparticles were synthesized by reduction of copper nitrate with hydrazine hydrate. The stabilizer is cetyltrimethyl ammonium bromide (CTAB, C<sub>19</sub>H<sub>42</sub>BrN) or mixture of CTAB and Polyvinylpyrrolidone (PVP). In comparison with our results reported previously [1, 2], this method produces pure copper nanoparticles at room temperature without the use of any extra inert gas. The effects of variables such as hydrazine concentration, pH, concentration of CTAB and PVP on the growth of copper nanoparticles have been examined.

*Keywords:* copper nanoparticles; hydrazine reduction method.

## 1. INTRODUCTION

Copper nanoparticles had been extensively studied due to their potentially technological applications such as in catalysis and lubricant fields [3 - 5]. Conventionally, copper nanoparticles could be prepared by a variety of methods, including gas evaporation technique, liquid-phase precipitation, pulsed laser ablation, aqueous solution reduction, an  $\gamma$ -radiation hydrothermal method [1 - 5]. In our study, hydrazine hydrate was used as the reducing agent to investigate the preparation of copper nanoparticles in water with the presence of surfactant CTAB or mixture of CTAB and PVP.

## 2. EXPERIMENTAL

### 2.1. Materials

Copper (II) nitrate hydrate [Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O], Merck, 99 %; Hydrazine hydrate [N<sub>2</sub>H<sub>4</sub>·2H<sub>2</sub>O], Merck, 99 %; Hexadecyltrimethylammoniumbromide (or cetyltrimethyl ammonium bromide, C<sub>19</sub>H<sub>42</sub> NBr), Himedia, India, 99.9 %; Polyvinylpyrrolidone PVP, M =

55,000 g/mol; Ammonia solution was purchased China. All chemicals were used as received without further purification.

## 2.2. Synthesis

In a typical synthesis process, the solution containing  $10^{-3}$  M copper nitrate and  $10^{-2}$  M CTAB with additional  $\text{NH}_3$  to adjust solution pH. Hydrazine hydrate 0.1 M was added and kept at room temperature with continuous stirring. As the reaction proceeded within 20 min, the solution color changed from colorless to light yellow to orange to brown and finally to red color, which confirmed the formation of metallic copper nanoparticles.

## 2.3. Characterization

The UV-Vis absorption spectrum of the product solution was measured by Jasco V670, Applied Physical Chemical Lab-University of Science, VNU HCM city. TEM images were taken by JEM-1400, University of Technology-VNU HCM City. XRD were characterized using D8 advanced Bragg X Ray powder diffraction with  $\text{Cu K}\alpha$  radiation.

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of pH solution

Table 1. Effect of pH solution on Cu nanoparticles

Sample	$\text{Cu}(\text{NO}_3)_2$ (M)	CTAB (M)	PVP	pH	$\text{N}_2\text{H}_4$ (M)	Time (min)	Abs.	Peak (nm)
a1	$10^{-3}$	$10^{-2}$		5	0.10	15	1.48	566
a2	$10^{-3}$	$10^{-2}$		6	0.10	15	1.48	565
a3	$10^{-3}$	$10^{-2}$		7	0.10	15	1.52	567
a4	$10^{-3}$	$10^{-2}$		8	0.10	15	1.53	564
a5	$10^{-3}$	$10^{-2}$		9	0.10	15	2.14	571
a6	$10^{-3}$	$10^{-2}$		10	0.10	20	2.76	569
a7	$10^{-3}$	$10^{-2}$		11	0.10	80	2.15	576
b1	$10^{-3}$	$10^{-2}$	$10^{-2}$	5	0.10	15	1.54	567
b2	$10^{-3}$	$10^{-2}$	$10^{-2}$	6	0.10	20	1.52	566
b3	$10^{-3}$	$10^{-2}$	$10^{-2}$	7	0.10	20	1.54	566
b4	$10^{-3}$	$10^{-2}$	$10^{-2}$	8	0.10	20	1.67	568
b5	$10^{-3}$	$10^{-2}$	$10^{-2}$	9	0.10	20	1.59	566
b6	$10^{-3}$	$10^{-2}$	$10^{-2}$	10	0.10	25	1.85	566
b7	$10^{-3}$	$10^{-2}$	$10^{-2}$	11	0.10	80	1.59	567

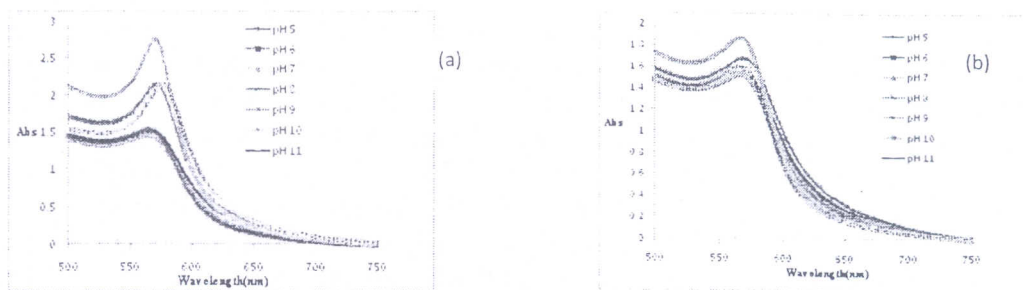


Figure 1, (a) UV-Vis of the sample a1-a7 with the protecting agent CTAB 0.10 M; (b) UV-Vis of sample b1-b7 with the mixture of protecting agent CTAB 0,10M and PVP 0.10 M

The effect of solution pH on the formation of copper nanoparticles was examined with pH changing from 5 to 11. The pH was adjusted with the addition of liquid ammonia. The results were summarized in table 1, Fig. 1(a) and Fig. 1(b). Fig. 1(a) showed the UV-Vis of the samples a1, a2, a3, a4, a5, a6, a7 (with the protecting agent CTAB 0.10M) corresponding with the pH 5, 6, 7, 8, 9, 10, 11, 12, respectively. In the case, UV-Vis of sample a6 at pH of 10 had the lowest peak position, 569 nm (i.e, small-sized nanoparticles to the Mie Law) and obtained the highest absorption, 2.76 (i.e., the density of nanoparticles is high). Fig. 1(b) illustrated showed that the UV-Vis of the samples b1, b2, b3, b4, b5, b6, b7 (with the mixture of protecting agent CTAB 0.10 M and PVP 0.10 M) corresponding with the pH 5, 6, 7, 8, 9, 10, 11, 12, respectively. In the case, UV-Vis of sample b6 at pH of 10 had the lowest peak position, 566 nm (small-sized nanoparticles) and obtained the highest absorption, 1.85 (the density of nanoparticles is high).

### 3.1. Effect of hydrazine concentration

The effect of hydrazine concentration on the growth of copper nanoparticles was investigated with varying the hydrazine concentration from 0.025 M to 1.250 M at pH = 10 with stirring. The results were summarized in table 2, Fig. 2(a) and Fig. 2(b). Fig. 2(a) showed the UV-Vis of the samples c1, c2, c3, c4, c5 (with the protecting agent CTAB 0.10 M) corresponding to the concentration of hydrazine 0.125 M; 0.100M, 0.075 M, 0.025 M, respectively. Fig. 2(b).

Table 2. Effect of hydrazine concentration on copper nanoparticle solution

Sample	Cu(NO <sub>3</sub> ) <sub>2</sub> (M)	CTAB (M)	PVP	pH	N <sub>2</sub> H <sub>4</sub> (M)	Time (min)	Abs	Peak (nm)
c1	10 <sup>-3</sup>	10 <sup>-2</sup>		10	0.125	15	2.32	569
c2	10 <sup>-3</sup>	10 <sup>-2</sup>		10	0.100	20	2.76	569
c3	10 <sup>-3</sup>	10 <sup>-2</sup>		10	0.075	60	1.76	563
c4	10 <sup>-3</sup>	10 <sup>-2</sup>		10	0.050	60	1.74	565
c5	10 <sup>-3</sup>	10 <sup>-2</sup>		10	0.025	-	-	-
d1	10 <sup>-3</sup>	10 <sup>-2</sup>	10 <sup>-2</sup>	10	0.125	25	1.88	575
d2	10 <sup>-3</sup>	10 <sup>-2</sup>	10 <sup>-2</sup>	10	0.100	25	1.85	566
d3	10 <sup>-3</sup>	10 <sup>-2</sup>	10 <sup>-2</sup>	10	0.075	30	1.79	567
d4	10 <sup>-3</sup>	10 <sup>-2</sup>	10 <sup>-2</sup>	10	0.050	50	1.62	569
d5	10 <sup>-3</sup>	10 <sup>-2</sup>	10 <sup>-2</sup>	10	0.025	-	-	-



Shown that the UV-Vis of the samples d1, d2, d3, d4, d5 (with the mixture of protecting agent CTAB 0.10 M and PVP 0.1 M) corresponding to the concentration of hydrazine 0.125 M; 0.100 M, 0.075 M, 0.025 M, respectively. The results from UV-Vis spectra showed that the more the concentration of reductant increased (from 0.050M to 0.1M), the more the absorption of peak also increased gradually (1.74, 1.76, 2.76 with the sample c4,c2,c3,c1 or 1.62,1.79,1.85,1.88 with the sample d4,d3,d2,d1). To sample c2 and sample d2, having the hydrazin concentration of 0.1 M, the synthesis of copper nanoparticles happened easily and data of UV-Vis showed that the peak position got the lowest value (569 nm with sample c2 and 566 nm with sample d2) and the absorption intensity was high (2.76 with sample c2 and 1.85 with sample d2). Therefore, the concentration of hydrazin 0.100 M is one of best choice to synthesize copper nanopartilles.

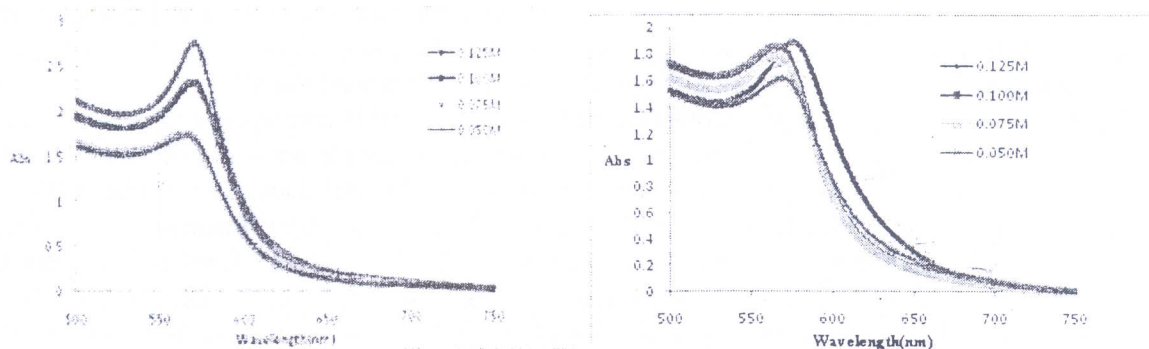


Figure 2. (a) UV-Vis of the samples c1-c5 (with the protecting agent CTAB 0.10 M) (b). UV-Vis of the samples d1 - d5 (with the mixture of protecting agent CTAB 0.10 M and PVP 0.1 M)

### 3.3. XRD analysis

Results from XRD patterns showed the influence of pH on the purity of copper nanoparticles. Copper colloidal solutions (a1 with pH of 5; a6 with pH of 10) were coating on the glass of microscopy by spin coating and baked at 300 °C under nitrogen condition. The X-ray diffraction patterns of sample a1 which were corresponded to crystalline copper characteristic peaks with a face-centered-cubic (fcc) crystal structure at 2θ value of 43,60; 50,70 and 74,50 representing (111), (200) and (220) planes of fcc structure of copper (Fig. 3a).

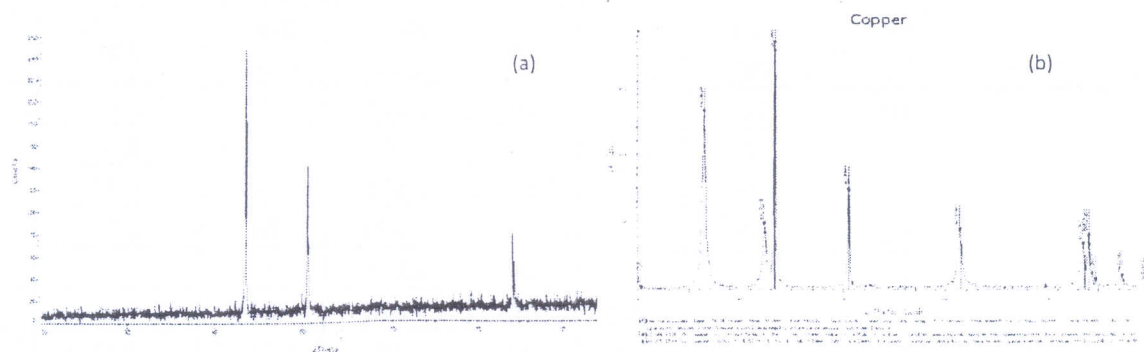


Figure 3. (a) XRD pattern of a6 (pH = 10) in CTAB solution with stirring (b) XRD pattern of a1(pH = 5) in CTAB solution with stirring

The X-ray diffraction patterns of sample a1 (Fig. 3b) showed that besides copper nanoparticles possessing crystalline copper characteristic peaks with a face-centered-cubic (fcc) crystal structure at  $2\theta$  value of 43,60; 50,70 and 74,50 representing (111), (200) and (220) planes of fcc structure of copper, there were also peaks which characterized copper nanoparticles  $\text{Cu}_2\text{O}$ , including peak 37, 42, 61, 73 representing (111), (200) and (220) and (311) planes of fcc structure of copper oxide.

### 3.4. TEM Images

Results from TEM images showed the influence of protecting agents on shapes and sizes of copper nanoparticles. With protecting agent CTAB 0.01 M, the sample c2 had been stable over 2 months since the time point of this study. Nevertheless, nanoparticles were rather large with the distribution from 20 to 70 nm, concentrating from 20 to 50 nm (Fig. 4a). With the mixture of protecting agent CTAB 0.01 M and PVP 0.01 M, the sample had a small size of below 10 nm, concentrating from 6 to 8 nm. However, the sample was not stable and cloudy after 1 week (Fig. 4b). It is perhaps that high concentration of PVP made its chain roll on together then after a certain time, it would not protect copper nanoparticles well. With the mixture of protecting agent CTAB 0.01 M and PVP 0.01 M, sizes of nanoparticles were small under 10nm, concentrating from 4 to 6 nm. The stability of this sample was high after 2 months since the time point of this study (Fig. 5).

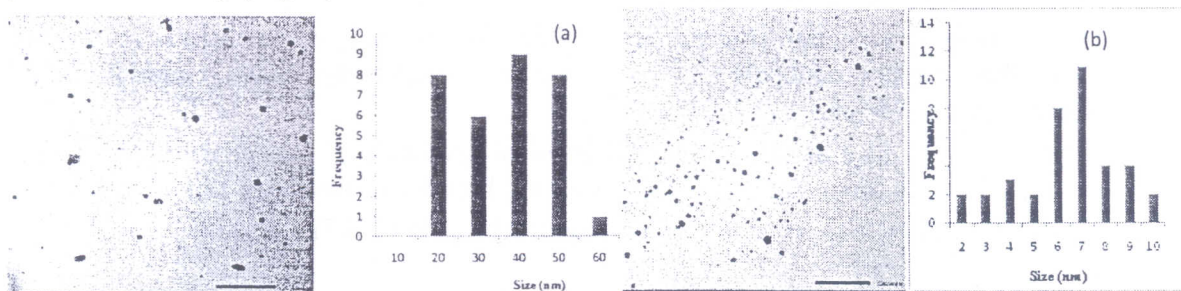


Figure 4. (a) TEM image (scale of 500 nm) and distribution of particle size of the sample c2 (protecting agent CTAB 0.01 M)  
 (b) TEM image (scale of 100nm) and distribution of particle size of the sample d2 (mixture of protecting agent CTAB 0.01 M and PVP 0.01 M)

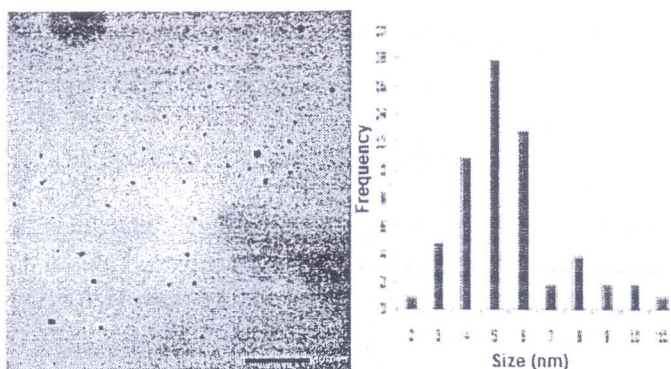


Figure 5 TEM image (scale of 100 nm) and distribution of particle size of the sample c2 (mixture of protecting agent CTAB 0.01 M and PVP 0.001 M)



#### 4. CONCLUSIONS

Successfully synthesized copper nanoparticle solution by reduction method with the hydrazine reducing agent with the protecting agent CTAB and mixture of CTAB and PVP. The XDR pattern proved that at pH of 10, pure copper nanoparticles are received while at pH of 5, extra diffraction peaks attributed to copper oxide. TEM Images showed the influence of protecting agents on shapes and sizes of copper nanoparticles. The mixture of protecting agents, CTAB 0.01 M and PVP 0.001 M are suitable to synthesize stable copper nanoparticle solution.

The synthesis of copper nanoparticles by hydrazine hydrate reduction method is a simple method with low cost for mass production.

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#### TÓM TẮT

#### TỔNG HỢP HẠT NANO ĐỒNG TẠI NHIỆT ĐỘ PHÒNG BẰNG PHƯƠNG PHÁP KHỬ VỚI HYDRAZIN

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Hạt nano đồng được tổng hợp bằng phương pháp khử đồng nitrate với chất khử là hydrazin hydrat. Chất ổn định là cetyltrimethyl ammonium bromid (CTAB, C<sub>19</sub>H<sub>42</sub>BrN) hay hỗn hợp của CTAB và Polyvinylpyrrolidon (PVP). So sánh các kết quả nghiên cứu trước đây [1, 2] cho thấy phương pháp này tổng hợp hạt nano đồng ở nhiệt độ phòng với hiệu suất cao không sử dụng điều kiện khí trơ. Ảnh hưởng của nồng độ hydrazin, CTAB, PVP và điều kiện pH đến sự hình thành hạt nano đồng cũng được khảo sát trong nghiên cứu này.

*Từ khoá:* hạt nano đồng, phương pháp khử với hydrazin