Preparation of Cu nanoparticles with ascorbic acid by aqueous solution reduction method

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Abstract: Cu nanoparticles were prepared by reducing Cu^{2+} ions with ascorbic acid through aqueous solution reduction method. The effects of solution pH and average size of Cu_2O particles on the preparation of Cu nanoparticles were investigated. Cu particles were prepared at pH 3, 5 or 7, with the smallest Cu particles obtained at pH 7. However, Cu particles could not be prepared at pH 9 or 11. The average size of Cu_2O particles can affect that of Cu particles. Larger Cu_2O particles result in larger Cu particles. In addition, experiments were conducted to explore the reaction process by measuring the X-ray diffraction (XRD) patterns of specimens collected at different time points during the reaction. It was found that $Cu(OH)_2$ was initially formed as a precursor, followed by the formation of Cu_2O, which was finally reduced to Cu particles.
Key words: Cu nanoparticles; aqueous solution reduction method; ascorbic acid; intermediate product

1 Introduction

Cu nanoparticles currently attract significant research attention owing to their widespread application in powder metallurgical materials and electronic circuits. Furthermore, because of their high electrical conductivity and chemical activity, Cu nanoparticles can replace Au and Ag in some potential applications such as conductive pastes and catalysts. There are many well-known methods for the preparation of Cu nanoparticles including the hydrothermal reduction method [1], supercritical technique [2], radiation method [3], microemulsion technique [4], sonochemical reduction method [5], laser ablation technique [6], metal vapor synthesis method [7], vacuum vapor deposition [8] and aqueous solution reduction method [9]. Among these methods, the aqueous solution reduction method is the most widely employed, due to the advantages including high yield and quality of particles, simplicity of operation, limited equipment requirements, and ease of control. Ascorbic acid is a reductant with a weak reducing ability. As a result, the reaction driving force is low [10], and it is difficult for the Cu particles to aggregate and grow. Although much research has been conducted in this area [11−14], the main focus was the

optimization of reaction conditions. The reaction mechanism was rarely reported. In this research, the focus is to investigate the mechanism of reaction process.

2 Experimental

All reagents used in the experiments were of analytical grade and obtained from Nacalai Tesque (Kyoto). The flowchart of the experimental process is shown in Fig. 1. 100 mL 0.2 mol/L $CuSO_4$ solution and 40 mL 1.0 mol/L ascorbic acid were prepared before the experiments. Ar gas was bubbled through both solutions for 30 min, and the solution pH values were then adjusted to be the same using H_2SO_4 and NaOH solutions. Polyvinylpyrrolidone (PVP) was added to the $CuSO_4$ solution as a dispersant. Ascorbic acid was added into the beaker containing the solution at 333 K under stirring with a magnetic rod. The color of the mixture changed from blue to brown, indicating the precipitation of Cu particles. When the reaction was complete, a small quantity of the slurry formed was collected for size distribution measurements with an electrophoretic light scattering spectrophotometer (ELS−8000NS, Otsuka Electronics Co. Ltd, Japan). Cu particles formed by precipitation were separated by centrifugation, washed

several times with distilled water and ethanol, and finally put in a vacuum stove (vacuum degree: −0.1 MPa) at room temperature for several days. Scanning electron microscopy (SEM) images of the specimens were obtained using a scanning electron microscope (S−800, Hitachi Co. Ltd, Japan) and XRD patterns of the specimens were recorded using an X-ray diffractometer (XRD−6000, Shimadzu Co. Ltd, Japan) with Cu K$_\alpha$ radiation.
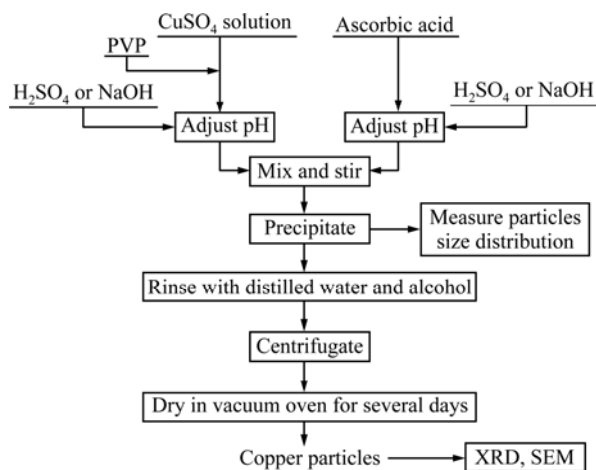

Fig. 1 Flowchart of experimental process

3 Results and discussion

3.1 Effect of solution pH on preparation of Cu nanoparticles

The effect of solution pH on the preparation of Cu nanoparticles was investigated by using the 0.2 mol/L CuSO$_4$ solution, 1.0 mol/L ascorbic acid, and 15 mmol/L PVP while the solution pH was altered to 3, 5, 7, 9 and 11 in sequence. The SEM images and XRD patterns of the Cu particles are shown in Figs. 2, 3 and 4. The results show that Cu(OH)$_2$ was formed as precursor at pH 5 or 7, whereas CuO was formed as precursor at pH 9 or 11. After agitation for 10 min, deposits could be obtained at every pH value. However, only when the solution pH was 3, Cu particles could be prepared within 10 min. When the solution pH was increased from 5 to 11, Cu$_2$O was prepared within 10 min. To obtain Cu particles, the agitation time had to be extended to 4 h.

The XRD patterns of Cu particles obtained after agitation for 4 h are shown in Fig. 5. Cu particles can be obtained when solution pH was 5 or 7. The average size of Cu particles obtained at pH 5 or 7 was smaller than those prepared at pH 3. And the average size decreased as the solution pH increased from 5 to 7. In Cu(OH)$_2$ solution, the Cu^{2+} concentration can be calculated according to equation (1). When solution pH was 7, the

Cu^{2+} concentration was very small (1.58×10^{-5} mol/L). As a result, small Cu particles can be obtained. When the solution pH was increased to 9 or 11, Cu particles could not be obtained, although Cu$_2$O was forms after a long reaction time (4 h). This is because CuO forms as precursor and it is difficult to reduce to Cu$_2$O. In contrast, when solution pH was 3, Cu particles could be prepared within 10 min. When solution pH was 5 or 7, Cu particles could be obtained after agitation for 4 h. The smallest Cu particles could be obtained at pH 7 because Cu^{2+} concentration was very low. When solution pH was 9 or 11, Cu particles could not be prepared. Hence, the optimal reaction pH is suggested to be 7.
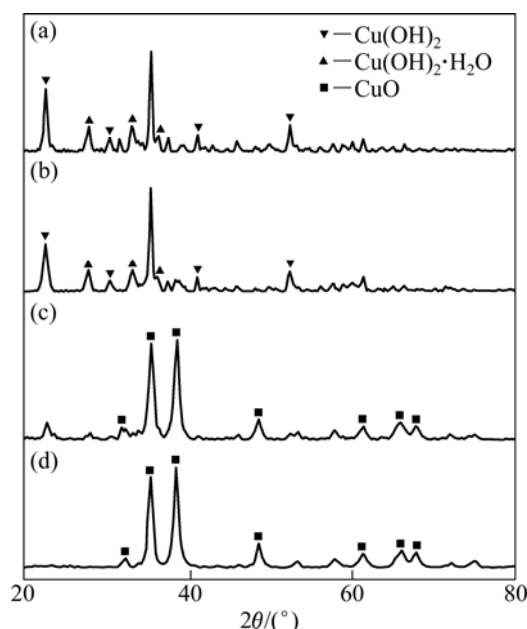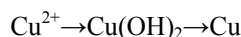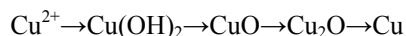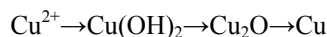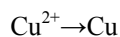
$$\lg[Cu^{2+}]=9.2-2pH \tag{1}$$

Fig. 2 XRD patterns of deposits before reaction at different pH values: (a) pH 5; (b) pH 7; (c) pH 9; (d) pH 11

3.2 Reduction process at pH 7

Four possible reaction processes may contribute to the formation of Cu particles as follows.

Cu^{2+}→Cu

Cu^{2+}→Cu(OH)$_2$→Cu$_2$O→Cu

Cu^{2+}→Cu(OH)$_2$→CuO→Cu$_2$O→Cu

Cu^{2+}→Cu(OH)$_2$→Cu

A series of experiments were conducted to study the reduction process during the preparation of Cu particles. From a mixture of 0.2 mol/L Cu^{2+}, 1.0 mol/L ascorbic acid, and 15 mmol/L PVP at pH 7, the specimens at specific time points (0, 10, 30, 60, 90, 120, 240 min) during the reaction were collected and their XRD patterns were measured. The results are shown in Fig. 6. The XRD patterns show that Cu^{2+} ions were initially
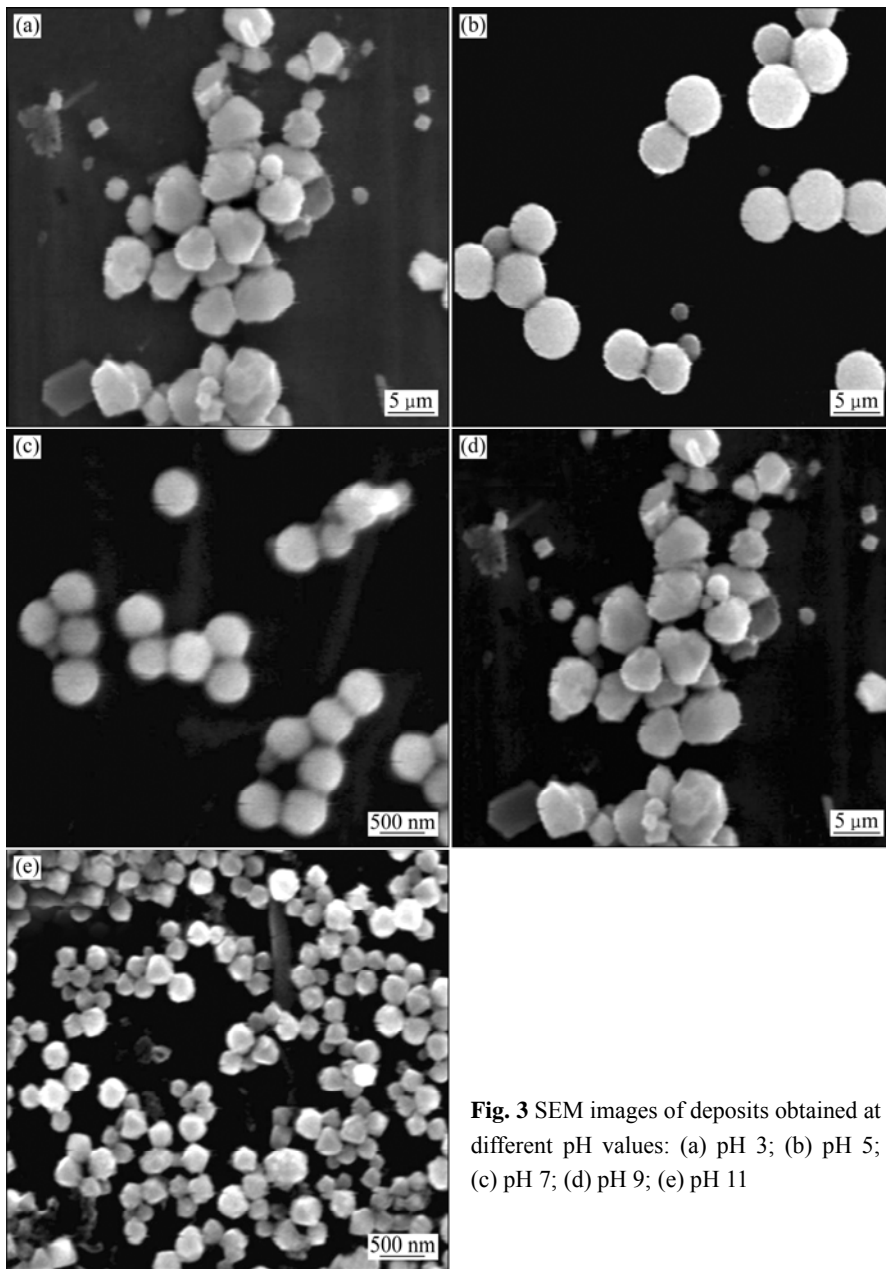
Fig. 3 SEM images of deposits obtained at different pH values: (a) pH 3; (b) pH 5; (c) pH 7; (d) pH 9; (e) pH 11
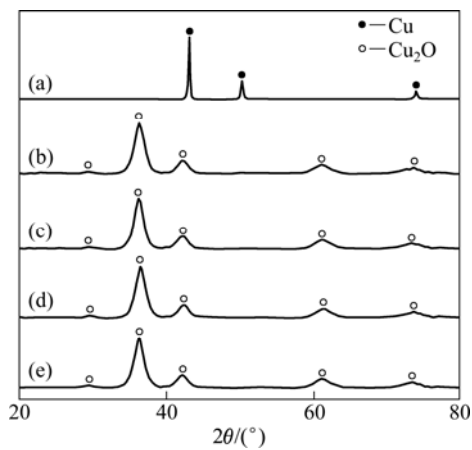

Fig. 4 XRD patterns of deposits agitated for 10 min at different pH values: (a) pH 3; (b) pH 5; (c) pH 7; (d) pH 9; (e) pH 11
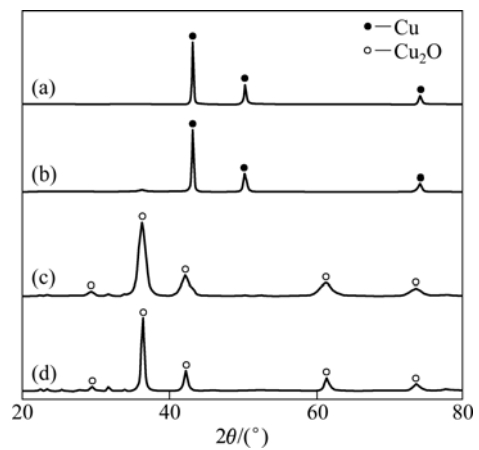

Fig. 5 XRD patterns of deposits agitated for 4 h at different pH values: (a) pH 5; (b) pH 7; (c) pH 9; (d) pH 11

transformed to $Cu(OH)_2$ as precursor, and then $Cu(OH)_2$ was reduced to Cu_2O by ascorbic acid. Cu_2O was finally reduced to Cu particles. Hence, Cu_2O is an intermediate product. The reduction process can be represented as follows.

$$Cu(OH)_2+C_6H_8O_6 \rightarrow Cu_2O+C_6H_6O_6+H_2O \qquad (2)$$

$$Cu_2O+C_6H_8O_6 \rightarrow Cu+C_6H_6O_6+H_2O \qquad (3)$$
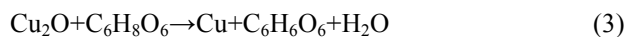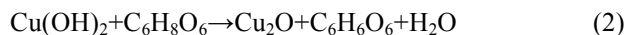
To prove this finding, the reaction potential was recorded using a potentiostat (Habf 501, Hokuto Denko Co. Ltd, Japan). Cu wire (d1.0 mm) and Ag/AgCl saturated KCl electrodes were used as the working and reference electrodes, respectively [15]. The results are shown in Fig. 7. As the reaction progressed, the potential moved from right to left. This potential graph can prove the validity of reactions (2) and (3).
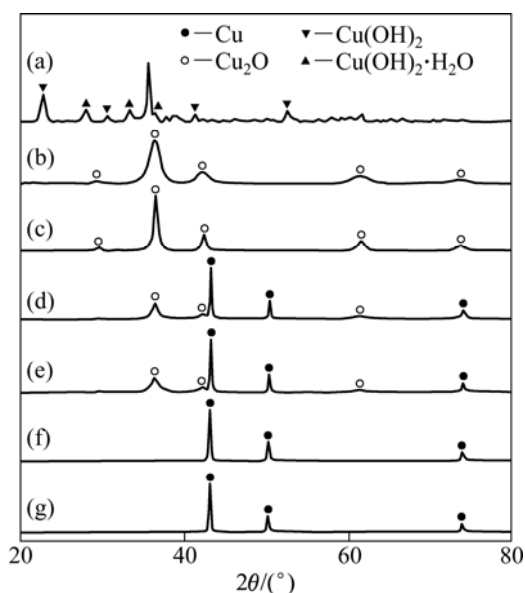

Fig. 6 XRD patterns of Cu particles at different time points: (a) 0 min; (b) 10 min; (c) 30 min; (d) 60 min; (e) 90 min; (f) 120 min; (g) 240 min
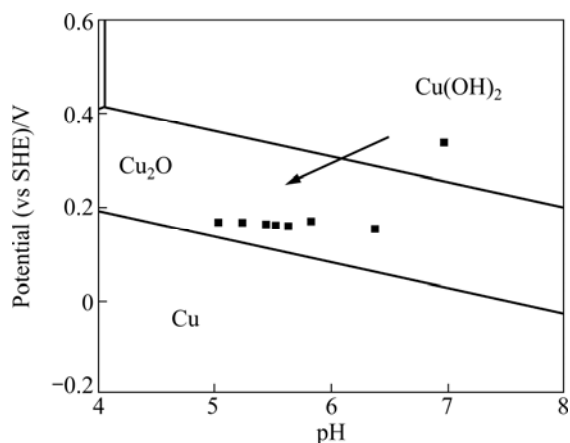

Fig. 7 Potential change with pH during reduction reaction process at 333 K ($c(Cu^{2+})$=0.2 mol/L)

3.3 Effect of Cu_2O particles size on preparation of Cu nanoparticles

According to section 3.2, Cu_2O was formed as an intermediate product during the reaction. To explore the effect of Cu_2O particles size on the final Cu particles size, a series of experiments were conducted. The experimental conditions are shown in Table 1. Solution B was added into solution A and the mixture was agitated for 10 min. The deposits were then centrifuged, rinsed with distilled water and ethanol, and put in a vacuum stove at room temperature for several days. The result is shown in Fig. 8. According to the XRD pattern, the deposits obtained under all conditions were Cu_2O particles. From the Cu_2O particles obtained under the three conditions (see Table 1), 0.715 g Cu_2O was dissolved in 50 mL distilled water, and 15 mmol/L PVP was added to the solution. The powders that can not dissolve in the solution was dispersed by an ultrasonic cleaner. Then, the pH of 1.0 mol/L ascorbic acid was adjusted to 7, and 20 mL of this pH-adjusted solution was added to Cu_2O solution. After agitation for 4 h at 333 K, the deposits were centrifuged, rinsed with ethanol, and put in a vacuum stove at room temperature for several days. The results are shown in Fig. 9. The XRD patterns show that Cu particles could be prepared under each condition listed in Table 1. The changes in the average diameter of particles were from 268 to 126 nm, from 300 to 157 nm and from 356 to 375 nm for conditions 1, 2 and 3, respectively. Furthermore, according to the SEM images, if we neglect the aggregation of particles, condition 1 resulted in the smallest particles, whereas condition 3 produced the largest particles. From these results, it can be concluded that the size of Cu_2O particles can influence that of Cu particles: larger Cu_2O particles result in larger Cu particles.
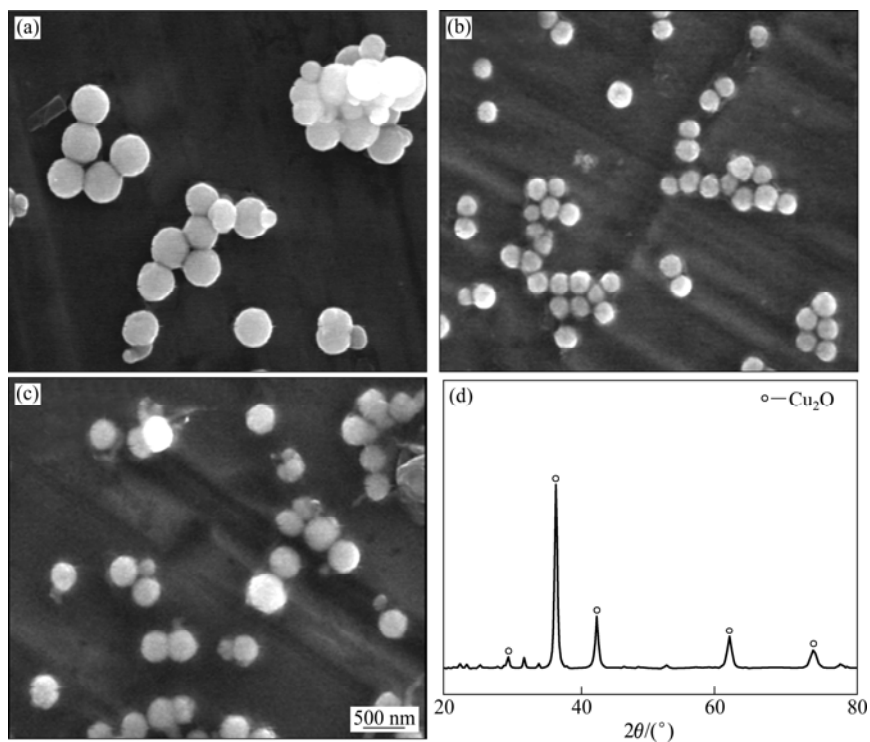
4 Conclusions

1) When the solution pH was 3, Cu particles could be prepared within 10 min, whereas when the solution pH was 5 or 7, Cu particles could only be obtained after agitation for 4 h. The Cu particles obtained at pH 7 were found to be the smallest because of the low Cu^{2+} concentration. When the solution pH was 9 or 11, Cu particles could not be prepared.

2) The reaction was found to proceed as follows. $Cu(OH)_2$ was formed from Cu^{2+} before the reaction and then reduced to Cu_2O by ascorbic acid. Cu_2O was finally reduced to Cu particles. Cu_2O is an intermediate product.

3) The average size of Cu_2O particles can affect that of Cu particles. Larger Cu_2O particles result in larger Cu particles.

Table 1 Reaction conditions for preparing Cu_2O particles

Condition	Solution A			Solution B		pH
	$c(CuSO_4)/(mol·L^{-1})$	V/mL	$c(PVP)/(mol·L^{-1})$	c(Ascorbic acid)/(mol·L^{-1})	V/mL	
1	0.5	40	0.015	2.5	40	7
2	0.2	40	0.015	1	40	7
3	0.2	300	0.015	1	120	7

Fig. 8 SEM images (a,b,c) and XRD pattern (d) of Cu_2O particles obtained under different conditions: (a) Condition 1; (b) Condition 2; (c) Condition 3; (d) XRD pattern
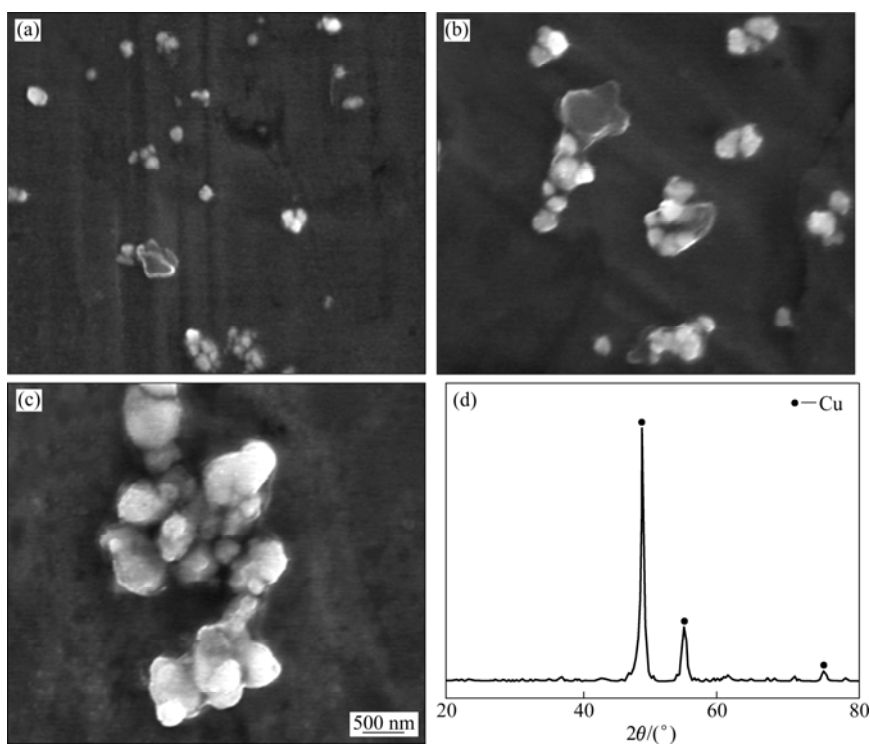
Fig. 9 SEM images (a,b,c) and XRD pattern (d) of Cu particles obtained under different conditions: (a) Condition 1; (b) Condition 2; (c) Condition 3; (d) XRD pattern

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通过水溶液还原法用抗坏血酸制备纳米铜颗粒

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摘　要：通过水溶液还原法用抗坏血酸还原 Cu^{2+} 制备纳米铜颗粒，并研究溶液 pH 和 Cu_2O 平均粒径对纳米铜颗粒制备的影响。在溶液 pH 值为 3、5 和 7 时，可制得铜颗粒，并且在 pH=7 时制得的铜颗粒粒径最小。在溶液 pH 为 9 和 11 时无法制得铜颗粒。Cu_2O 的平均粒径能影响铜粉的粒径。Cu_2O 的平均粒径越大，得到的铜颗粒越大。通过对反应过程中不同时间点收集的样品进行 XRD 分析，可探索出反应的进程。在反应过程中，$Cu(OH)_2$ 首先作为前驱体出现，然后被还原为 Cu_2O，最后被还原为铜颗粒。

关键词：纳米铜颗粒；水溶液还原法；抗坏血酸；中间产物

(Edited by YANG Hua)