

## Effects of reaction parameters on preparation of Cu nanoparticles via aqueous solution reduction method with NaBH<sub>4</sub>

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**Abstract:** The preparation of Cu nanoparticles by the aqueous solution reduction method was investigated. The effects of different reaction parameters on the preparation of Cu nanoparticles were studied. The optimum conditions for preparing well-dispersed nanoparticles were found as follows: 0.4 mol/L NaBH<sub>4</sub> was added into solution containing 0.2 mol/L Cu<sup>2+</sup>, 1.0% gelatin dispersant in mass fraction, and 1.2 mol/L NH<sub>3</sub>·H<sub>2</sub>O at pH 12 and 313 K. In addition, a series of experiments were performed to discover the reaction process. NH<sub>3</sub>·H<sub>2</sub>O was found to be able to modulate the reaction process. At pH=10, Cu<sup>2+</sup> was transformed to Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> as precursor after the addition of NH<sub>3</sub>·H<sub>2</sub>O, and then Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> was reduced by NaBH<sub>4</sub> solution. At pH=12, Cu<sup>2+</sup> was transformed to Cu(OH)<sub>2</sub> as precursor after the addition of NH<sub>3</sub>·H<sub>2</sub>O, and Cu(OH)<sub>2</sub> was then reduced by NaBH<sub>4</sub> solution.

**Key words:** Cu nanoparticles; NaBH<sub>4</sub>; Cu(OH)<sub>2</sub>; Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>; aqueous solution reduction method; precursor; reaction process

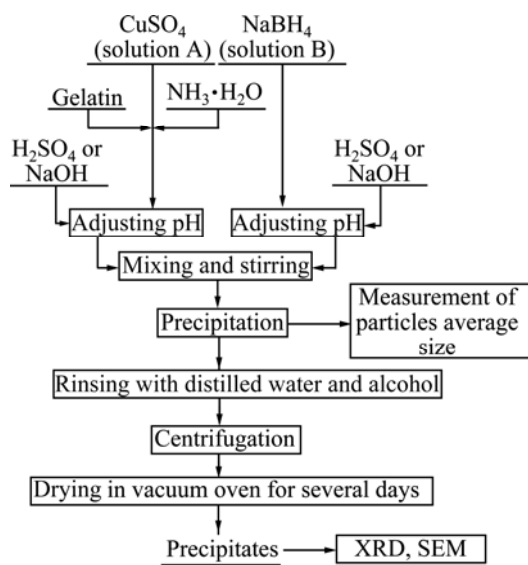
### 1 Introduction

The preparation of Cu nanoparticles has become an intensive area of study in material research because Cu nanoparticles are considered possible replacements for Au and Ag particles in several potential applications, such as catalyst and conductive paste [1–4]. Currently, there are many well-known preparation methods for Cu nanoparticles such as radiation [5], vacuum vapor deposition [6], microemulsion [7], mechanical chemistry [8], electrolysis [9], thermal reduction [10], laser ablation [11] and aqueous solution reduction [3]. Among these methods, radiation and vacuum vapor deposition methods require strict reaction conditions and large investment, which cause high-energy consumption but low yield rate. The mechanical chemistry method is simple and low-cost; however, particles prepared through this method are large and have low purity. The aqueous solution reduction method is widely used because of its advantages, such as simple equipment requirement, short technique flow, high yield rate and quality, and easy to be industrialized. In this method, NaBH<sub>4</sub> is used as a reductant because of its strong reducing ability [12], and NH<sub>3</sub>·H<sub>2</sub>O is added to the CuSO<sub>4</sub> solution to modify the

precursor, which may affect the reaction process. This method has been widely studied, but our focus is to discover the reaction process and investigate the effect of NH<sub>3</sub>·H<sub>2</sub>O on the reaction process. A series of contrast experiments were conducted to explore the optimum reaction conditions, and the reaction process was monitored by recording the SEM images and XRD patterns of the specimens obtained at various time points during the reaction.

### 2 Experimental

Analytical grade reagents obtained from Nacalai Tesque Inc. (Kyoto) were used in the experiments. The flowchart describing the experimental process is shown in Fig. 1. Before the experiments were conducted, 50 mL CuSO<sub>4</sub> and NaBH<sub>4</sub> solutions were prepared, respectively, and Ar gas was bubbled through both solutions for 30 min. The pH of each solution was adjusted to the same value using H<sub>2</sub>SO<sub>4</sub> or NaOH solutions. Gelatin was then added to the CuSO<sub>4</sub> solution as a dispersant. The NaBH<sub>4</sub> solution was added to the CuSO<sub>4</sub> solution with magnetic rod stirring. The color of the mixture changed from blue to brown, which indicated the precipitation of Cu particles. When the reaction was completed, small



**Fig. 1** Flowchart of experimental process

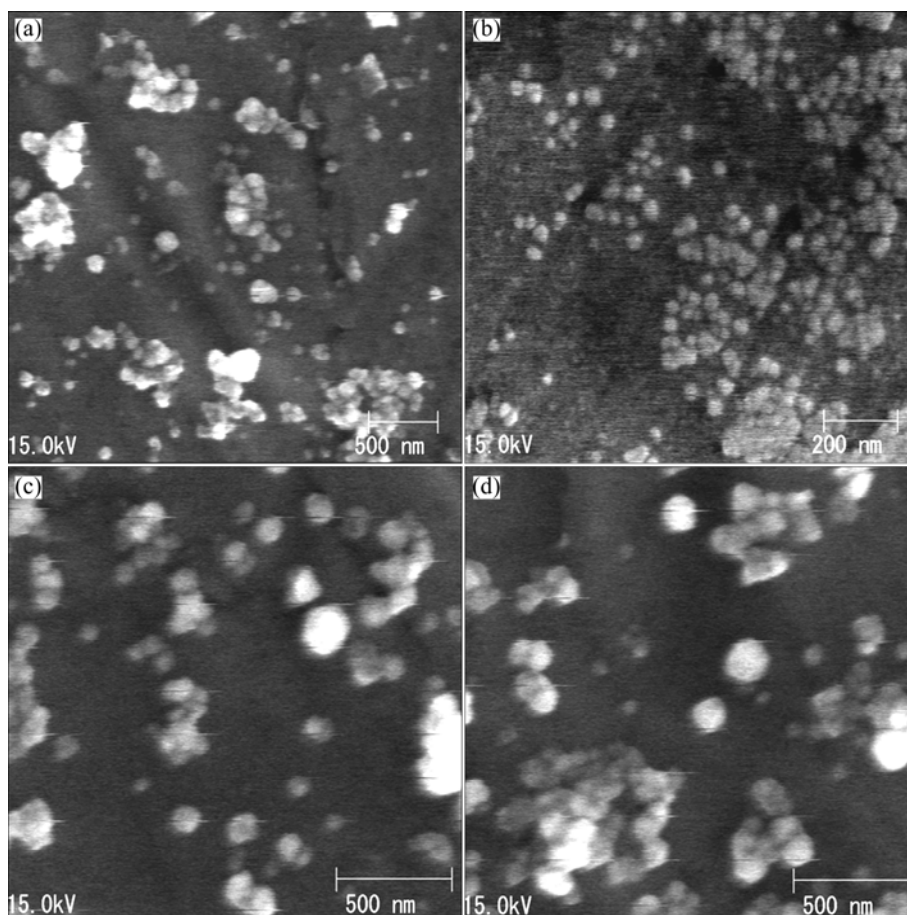
quantity of the slurry was collected for size distribution measurement using an electrophoretic light scattering spectrophotometer (ELS-8000NS, Otsuka Electronics Co. Ltd., Japan). Cu particles were separated via centrifugation, washed several times with distilled water

and ethanol, and finally dried in a vacuum stove at room temperature for several days. The SEM images of particles were obtained using a scanning electron microscope (S-800, Hitachi Co. Ltd., Japan) and the XRD patterns of the specimens were recorded using an X-ray diffractometer (XRD-6000, Shimadzu Co. Ltd., Japan) with Cu  $K_{\alpha}$  radiation.

### 3 Results and discussion

#### 3.1 Effect of solution temperature

Gelatin (1.0 mass %) was added to 50 mL of 0.2 mol/L  $\text{CuSO}_4$  (solution A), and 50 mL of 0.4 mol/L  $\text{NaBH}_4$  (solution B) was prepared. After the pH values of solutions A and B were adjusted to 10, solution B was immediately added to solution A. The solution temperatures were set as 298, 313, 323 and 333 K, respectively. Cu particles can be prepared after 10 min at each temperature. The SEM images of Cu particles are shown in Fig. 2. The smallest Cu particles (average size: 76 nm) were prepared at 313 K, and the average size of Cu particles increased with the rising of temperature. Generally speaking, the supersaturation of solution decreased with the increasing temperature. When the supersaturation of solution decreases, the crystal growth



**Fig. 2** SEM images of Cu particles obtained from solution at different temperatures: (a) 298 K, average particle size of 160 nm; (b) 313 K, average particle size of 76 nm; (c) 323 K, average particle size of 83 nm; (d) 333 K, average particle size of 89 nm

of nuclei is superior to the nucleation [9]. Hence, the average size of Cu particles increases with the temperature. Furthermore, the average size of Cu particles obtained at 298 K is 160 nm, which is the largest. And the coagulation is obvious. The reason is that gelatin will become solution when heated [13]. During this process, its structure transforms to a random coil shape, which can cause high dispersion effect. On the contrary, gelatin becomes colloidalized when cooled. As a result, gelatin cannot be well absorbed on the surface of Cu particles at a low temperature, which reduces its coagulation inhibiting ability. The colloidalization temperature is approximately 298 K. Hence, when gelatin is adopted as a dispersant, the solution temperature should be set over 298 K. By considering the average size of Cu particles, the optimal temperature is suggested as 313 K.

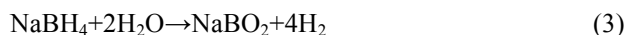
### 3.2 Effect of solution pH

When the solution pH is 10,  $\text{Cu}^{2+}$  will be transformed to  $\text{Cu}(\text{OH})_2$ . The  $\text{Cu}^{2+}$  concentration can be calculated from the solubility product constant of  $\text{Cu}(\text{OH})_2$  using equations (1) and (2). As shown in equation (2),  $\text{Cu}^{2+}$  concentration decreased with the increasing pH.  $\text{Cu}^{2+}$  concentration is a very important factor for the nucleation, growth-up and coagulation of nuclei. Thence, in this section the solution pH was altered to investigate its effect on the preparation of Cu particles.

$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{OH}^-]^2 = 1.6 \times 10^{-19} \text{ (mol}^3/\text{L}^3\text{)} \quad (1)$$

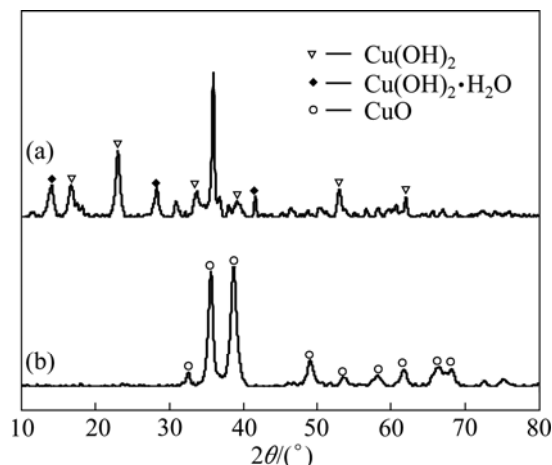
$$\lg[\text{Cu}^{2+}] = 9.2 - 2\text{pH} \quad (2)$$

As reported in a previous research [14], when the solution pH is below 9.5,  $\text{NaBH}_4$  can react with  $\text{H}_2\text{O}$  based on Eq. (3), which will weaken its reducing ability. Thus, the solution pH value was adjusted to 10 or 12 in the present experiment by fixing the other reaction conditions. Solution B was immediately added to solution A, and the reaction was performed at 313 K.

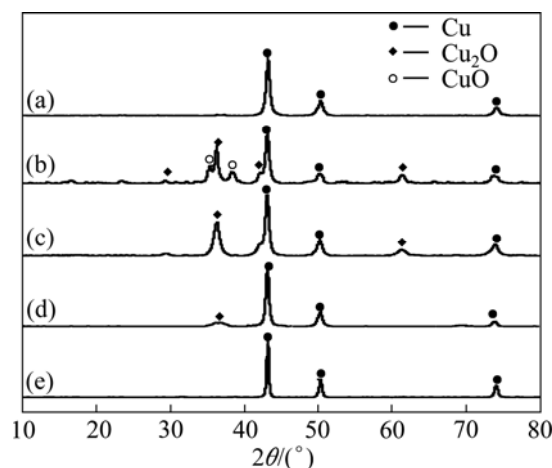


The XRD patterns of precursors formed at various pH values are shown in Fig. 3. The precipitates obtained at pH=10 consist of  $\text{Cu}(\text{OH})_2$  and  $\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , whereas those obtained at pH=12 are CuO. The XRD patterns of the final particles obtained at pH=10 and 12 are shown in Fig. 4. At pH=10, Cu particles were obtained at 10 min after reaction. At pH=12, the particles obtained at 10 min after reaction consist of Cu,  $\text{Cu}_2\text{O}$  and CuO, which indicated that the reaction was not complete. Thus, the reaction time was prolonged to 30 min and the experiment was repeated. After 30 min, CuO disappeared, whereas Cu and  $\text{Cu}_2\text{O}$  remained. The reaction was further prolonged to 2 h. As a result,  $\text{Cu}_2\text{O}$  disappeared,

and only Cu particles remained. In terms of size distribution, Cu particles obtained at pH 12 are smaller compared with those obtained at pH 10. Therefore, it is better to perform the experiment at pH 12.



**Fig. 3** XRD patterns of precipitates obtained from solution A with different pH values: (a) pH=10; (b) pH=12



**Fig. 4** XRD patterns of precipitates obtained from A+B solution with different pH values: (a) pH=10, 10 min; (b) pH=12, 10 min; (c) pH=12, 30 min; (d) pH=12, 60 min; (e) pH=12, 120 min

### 3.3 Effect of $\text{NH}_3 \cdot \text{H}_2\text{O}$ on reaction process

Based on the above conclusions, small Cu particles can be prepared at pH=12 and the optimal temperature for gelatin is 313 K. However, when the solution pH is 12, the reduction reaction time needs to be extended to 2 h because CuO was formed as precursor during the reaction process, which inhibited the reaction. Hence,  $\text{NH}_3 \cdot \text{H}_2\text{O}$  was added to  $\text{CuSO}_4$  solution to modify the precursor and change the reaction process.

Gelatin (1.0% in mass fraction) and 1.2 mol/L  $\text{NH}_3 \cdot \text{H}_2\text{O}$  were added to 50 mL of 0.2 mol/L  $\text{CuSO}_4$  (solution A). After the pH values of solutions A and B

were adjusted to 10 or 12, solution B was immediately added to solution A, and the reaction was maintained at 313 K. Cu particles could be prepared after 10 min under each condition.

The concentration distribution of  $\text{Cu}(\text{NH}_3)_i^{2+}$  at different pH values can be calculated via equations (4) and (5). The curves of  $\text{Cu}(\text{NH}_3)_i^{2+}$  concentration changed with solution pH value are shown in Fig. 5. As shown in Fig. 5,  $\text{Cu}^{2+}$  is transformed to  $\text{Cu}(\text{NH}_3)_i^{2+}$  when solution pH ranges from 8.5 to 11, whereas it is transformed to  $\text{Cu}(\text{OH})_2$  when solution pH ranges from 5 to 8 or over 11.

$$K_i = \frac{[\{\text{Cu}(\text{NH}_3)_i\}^{2+}]}{[\{\text{Cu}(\text{NH}_3)_{i-1}\}^{2+}][\text{NH}_3]} \quad (4)$$

$$\text{p}K_1 = -3.99, \text{p}K_2 = -3.34, \text{p}K_3 = -2.73, \text{p}K_4 = -1.97$$

$$K_{\text{NH}_3} = \frac{[\text{NH}_4^+]}{[\text{NH}_3][\text{H}^+]} \quad (5)$$

$$\text{p}K_{\text{NH}_3} = 9.26$$

At pH=10,  $\text{Cu}^{2+}$  is transformed to  $\text{Cu}(\text{NH}_3)_4^{2+}$  as precursor after the addition of  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . The reduction reaction is performed following equation (6). The average size of Cu particles is 55 nm, which is smaller than those obtained without the addition of  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . On the other hand,  $\text{Cu}^{2+}$  was transformed to  $\text{Cu}(\text{OH})_2$  as precursor after the addition of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  at pH=12. The reduction reaction was performed following equation (7). The average size of Cu particles is 37 nm, which are the smallest obtained in our experiments. As mentioned in section 3.2, the reduction reaction requires 2 h without the addition of  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . After  $\text{NH}_3 \cdot \text{H}_2\text{O}$  was added to prevent the formation of CuO, Cu particles can be prepared after 10 min.

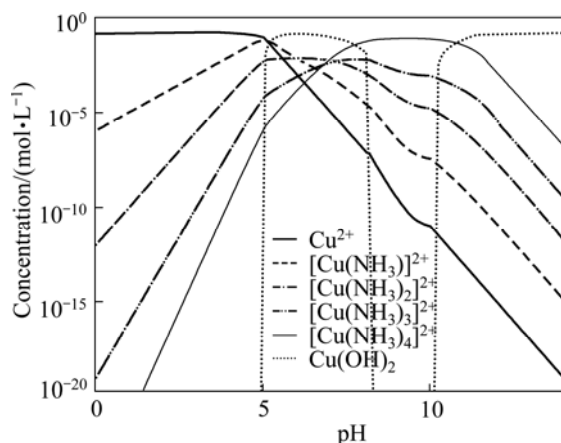
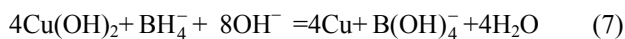
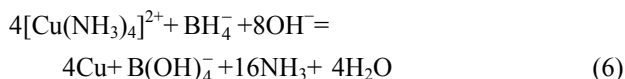
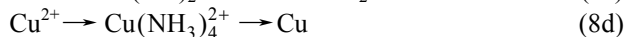
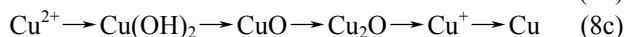


Fig. 5 Relationship between Cu ammoniate ion concentration and pH

### 3.4 Reaction process for preparation of Cu particles at pH=12

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



As discussed in section 3.2,  $\text{NaBH}_4$  can react with  $\text{H}_2\text{O}$  when the solution pH is below 9.5, which will lose its reducing ability. By using this character, when the reaction is conducted for a certain time, the solution pH is adjusted below 8, and the reaction can be stopped at that period. Then the precipitates obtained during the reaction can be collected. By measuring the SEM images and XRD patterns of these particles, the reaction process can be found out.

To identify the reaction process, a series of experiments were conducted. Under conditions of 0.2 mol/L  $\text{Cu}^{2+}$ , 0.4 mol/L  $\text{NaBH}_4$ , 1.0% gelatin in mass fraction, 1.2 mol/L  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , and pH=12, we recorded the SEM images and XRD patterns of specimens collected at several reaction time points (0, 0.5, 3, 5, 10, and 60 min) during the preparation of Cu particles. The results are shown in Figs. 6 and 7. The SEM images and XRD patterns showed that the majority of particles were rod-shaped  $\text{Cu}(\text{OH})_2$  during the initial stage of the reaction. After 5 min,  $\text{Cu}(\text{OH})_2$  disappeared and only Cu particles remained. The XRD pattern at 10 or 60 min was similar to that obtained at 5 min. This result indicates that the reduction reaction can be completed within 5 min. The XRD patterns also showed that all  $\text{Cu}^{2+}$  ions were transformed to  $\text{Cu}(\text{OH})_2$  before the two solutions were mixed.  $\text{Cu}(\text{OH})_2$  was then reduced to Cu particles by  $\text{NaBH}_4$ . The reaction process can be represented as follows:

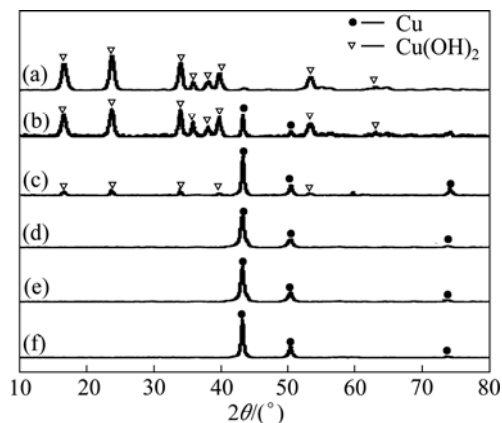
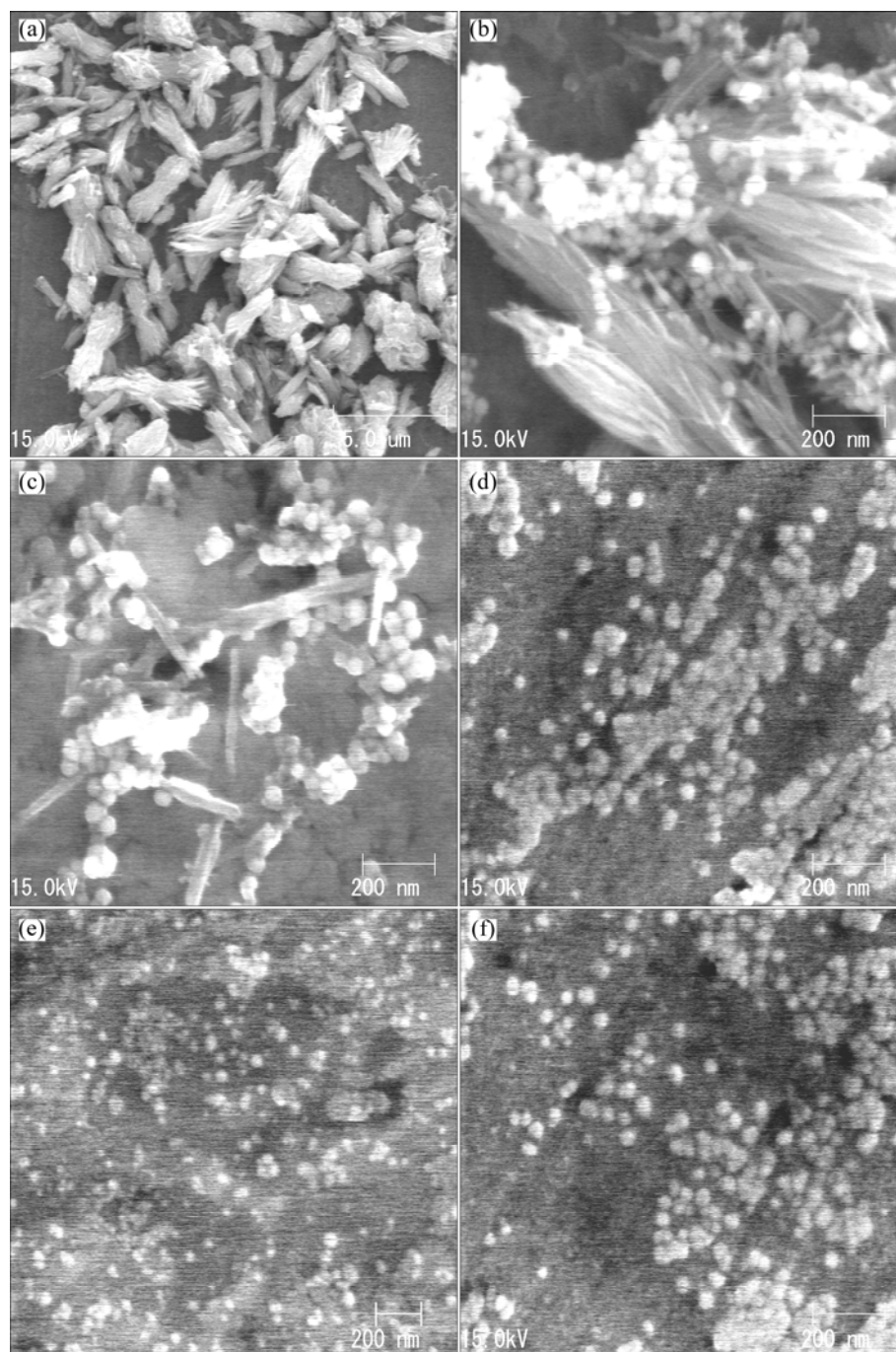


Fig. 6 XRD patterns of precipitates obtained from A+B solution at different time points: (a) 0; (b) 0.5 min; (c) 3 min; (d) 5 min; (e) 10 min; (f) 60 min



**Fig. 7** SEM images of Cu particles at different time points: (a) 0; (b) 0.5 min; (c) 3 min; (d) 5 min; (e) 10 min; (f) 60 min

## 4 Conclusions

1) The smallest Cu nanoparticles, with an average size of 37 nm, were prepared from a solution containing 0.2 mol/L  $\text{Cu}^{2+}$ , 0.4 mol/L  $\text{NaBH}_4$ , 1.0% gelatin in mass fraction, and 1.2 mol/L  $\text{NH}_3\cdot\text{H}_2\text{O}$ , at pH 12 and 313 K temperature.

2)  $\text{NH}_3\cdot\text{H}_2\text{O}$  could change the reaction process. When the solution pH was 10,  $\text{Cu}^{2+}$  was transformed to  $\text{Cu}(\text{NH}_3)_4^{2+}$  after the addition of  $\text{NH}_3\cdot\text{H}_2\text{O}$ .  $\text{Cu}(\text{NH}_3)_4^{2+}$  was subsequently reduced by  $\text{NaBH}_4$  solution. When the

solution pH was 12,  $\text{Cu}^{2+}$  is transformed to  $\text{Cu}(\text{OH})_2$  after the addition of  $\text{NH}_3\cdot\text{H}_2\text{O}$ .  $\text{Cu}(\text{OH})_2$  is then reduced by the added  $\text{NaBH}_4$  solution.

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## 通过水性还原法用 $\text{NaBH}_4$ 制备纳米铜颗粒过程中 反应参数对制备过程的影响

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**摘要:** 通过水溶液还原法制备纳米铜颗粒, 研究了不同反应条件对制备纳米铜的影响。制备纳米铜的最优条件是: 当溶液 pH 为 12、温度为 313 K、1% 的明胶作为分散剂时, 将 0.4 mol/L  $\text{NaBH}_4$  加入含有 1.2 mol/L 氨水的 0.2 mol/L  $\text{CuSO}_4$  溶液中。此外, 进行了一系列实验来模拟反应进程。结果表明, 氨水能改变反应进程。当溶液 pH 为 10 时, 氨水将  $\text{Cu}^{2+}$  转化为铜氨络合物, 然后被  $\text{NaBH}_4$  还原为铜颗粒。当溶液 pH 为 12 时, 氨水将  $\text{Cu}^{2+}$  转化为氢氧化铜, 然后被  $\text{NaBH}_4$  还原为铜颗粒。

**关键词:** 铜纳米颗粒;  $\text{NaBH}_4$ ; 氢氧化铜;  $\text{Cu}(\text{NH}_3)_4^{2+}$ ; 水溶液还原法; 前驱体; 反应进程

(Edited by YANG Hua)