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Preparation of Cu nanoparticles with $NaBH_4$ by aqueous reduction method

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Abstract: Cu nanoparticles were prepared by reducing Cu^{2+} ions with $NaBH_4$ in alkaline solution. The effects of $NaBH_4$ concentration and dripping rate on the formation of Cu nanoparticles were studied. The optimum conditions are found to be 0.2 mol/L Cu^{2+}, solution with pH=12, temperature of 313 K and 1% gelatin as dispersant, to which 0.4 mol/L $NaBH_4$ is added at a dripping rate of 50 mL/min. $NH_3{\cdot}H_2O$ is found to be the optimal complexant to form the Cu precursor. A series experiments were conducted to study the reaction process at different time points.

Key words: Cu nanoparticles; aqueous reduction method; precursor; reaction process

1 Introduction

In recent years, the preparation of Cu nanoparticles has become an intensive area of scientific research as Cu nanoparticles exhibit many excellent physical and chemical properties such as high electrical conductivity and chemical activity. Cu nanoparticles are considered possible replacements for Ag and Au particles in some potential applications, such as in catalysts and conductive pastes [1−4]. There are many well-known procedures for preparation of Cu nanoparticles, such as the radiation method [5], microemulsion technique [6], supercritical technique [7], thermal reduction [8], sonochemical reduction [9], laser ablation [10], metal vapor synthesis [11], vacuum vapor deposition [12] and aqueous reduction method [13]. Among these methods, aqueous reduction method is most widely employed because of its advantages such as simple operation, high yield and quality, limited equipment requirements and ease of control. Because of its strong reducing ability, $NaBH_4$ is widely used as a reductant for this aqueous reduction process. According to the previously reported research, much work has been done to explore the optimum conditions for preparation of copper nanoparticles [14]. However, the reaction mechanism has been seldom reported. In this research, the mechanism of reaction process was investigated based on the optimizing of the reaction conditions.

2 Experimental

All the 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. Prior to carrying out the experiments, 50 mL $CuSO_4$ solution and $NaBH_4$ solutions were prepared, and argon was bubbled through both the solutions for 30 min. Each pH value was adjusted to the same value using H_2SO_4 and NaOH solutions, respectively. Then 1% gelatin (mass fraction) was added into the $CuSO_4$ solution as a dispersant. The $NaBH_4$ solution was then added dropwise to the $CuSO_4$ solution in a beaker at 313 K with magnetic rod stirring. The color of the mixture was changed from blue to brown, indicating the precipitation of Cu nanoparticles. When the reaction was completed, a small quantity of the slurry was collected for size distribution measurements using an electrophoretic light scattering spectrophotometer (Model: ELS−8000NS, Otsuka Electronics Co. Ltd., Japan). Cu particles were formed by precipitation, which were separated by 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 were obtained by using a scanning electron microscope (model: S−800, Hitachi Co. Ltd., Japan) and the XRD patterns of the specimen were recorded using

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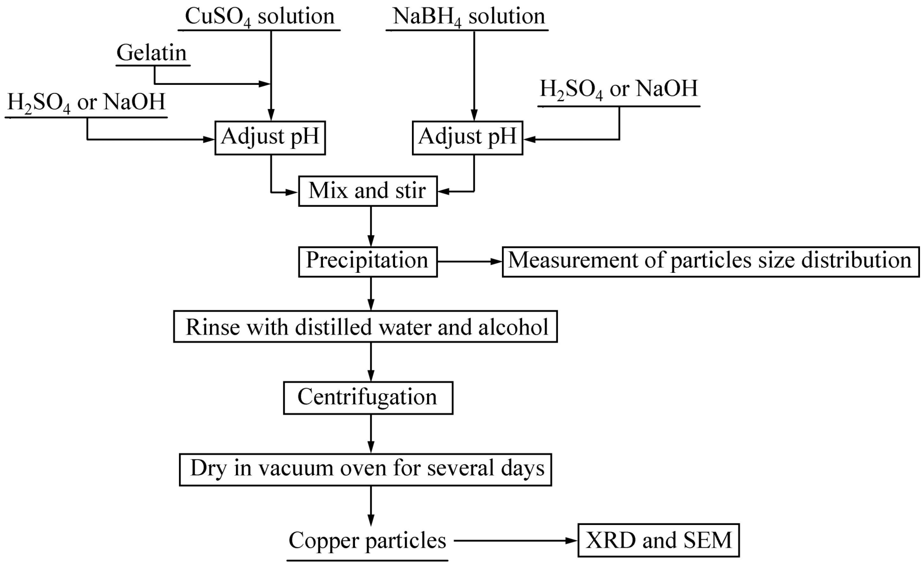


Fig. 1 Flow chart of experiment process

an X-ray diffractometer (model: XRD−6000, Shimadzu Co. Ltd., Japan) with Cu K_α radiation.

3 Results and discussion

3.1 Effect of $NaBH_4$ concentration on Cu nanoparticles preparation

In aqueous solution, the reaction takes place as

$$4Cu^{2+} + BH_4^- + 8OH^- = 4Cu + B(OH)_4^- + 4H_2O \quad (1)$$

In theory, the stoichiometric ratio of Cu^{2+} ions to $NaBH_4$ is 4:1. In the experiment, Cu^{2+} concentration is fixed at 0.2 mol/L, thus, the $NaBH_4$ concentration should ideally be 0.05 mol/L. With a fixed concentration (1%, mass fraction) gelatin as the dispersant and solution pH of 12, the effect of $NaBH_4$ concentration on the Cu particles was investigated. The results are shown in Fig. 2. It is observed that the average size of the Cu nanoparticles decreases with increasing $NaBH_4$ concentration. When the $NaBH_4$ concentration is 0.4 mol/L (8 times greater than the stoichiometric dosage), Cu nanoparticles with an average size of 37 nm are obtained. The XRD patterns show that at a low $NaBH_4$ concentration, the resultant particles contain $Cu(OH)_2$ and Cu_2O. At a higher $NaBH_4$ concentration, the $Cu(OH)_2$ contaminant disappears, but Cu_2O disappears only when the $NaBH_4$ concentration reaches several times the stoichiometric value. The analysis by XRD reveals that $Cu(OH)_2$ and Cu_2O contaminants are the intermediate products of the reduction process.

3.2 Effect of $NaBH_4$ dripping rate on Cu nanoparticles preparation

In the experiments, it is found that the dripping rate has a significant effect on the average size and shape of the Cu nanoparticles. The effect of the $NaBH_4$ dripping rate was investigated under constant condition of 0.2 mol/L Cu^{2+}, 0.4 mol/L $NaBH_4$, 1% gelatin and pH=12. The Cu particles were prepared with the $NaBH_4$ dripping rate of 5 and 50 mL/min, respectively. The results of this experiment are shown in Fig. 3. The average size of Cu particles prepared at a dripping rate of 5 mL/min is larger than that obtained at 50 mL/min. Traces of $Cu(OH)_2$ are also found, indicating that the reduction reaction is incomplete. The Cu nanoparticles obtained at dripping rate of 50 mL/min are smaller due to the occurrence of explosive nucleation when the two solutions are combined. According to the classical theory of nucleation, formation of Cu nanoparticles usually undergoes three stages: pre-nucleation, nucleation and crystal nucleus growth [15]. Explosive nucleation involves the generation of a large number of nuclei during the initial stages of nucleation. Since most of the Cu^{2+} ions are consumed for nucleation, the aggregation is limited. Thus, Cu nanoparticles with very small size can be obtained.

3.3 Effect of complexant on Cu nanoparticles preparation

Appropriate complexants in the $CuSO_4$ solution could not only eliminate the agglomeration of the Cu particles, but also change the morphology of the resultant particles. In this work, three types of complexants were adopted in the experiments, $NH_3 \cdot H_2O$, potassium sodium tartrate ($KNaC_4H_4O_6$) and trisodium citrate ($C_6H_5O_7Na_3$). The reduction reactions can be represented by the following equations.

When $NH_3 \cdot H_2O$ is adopted as complexant,

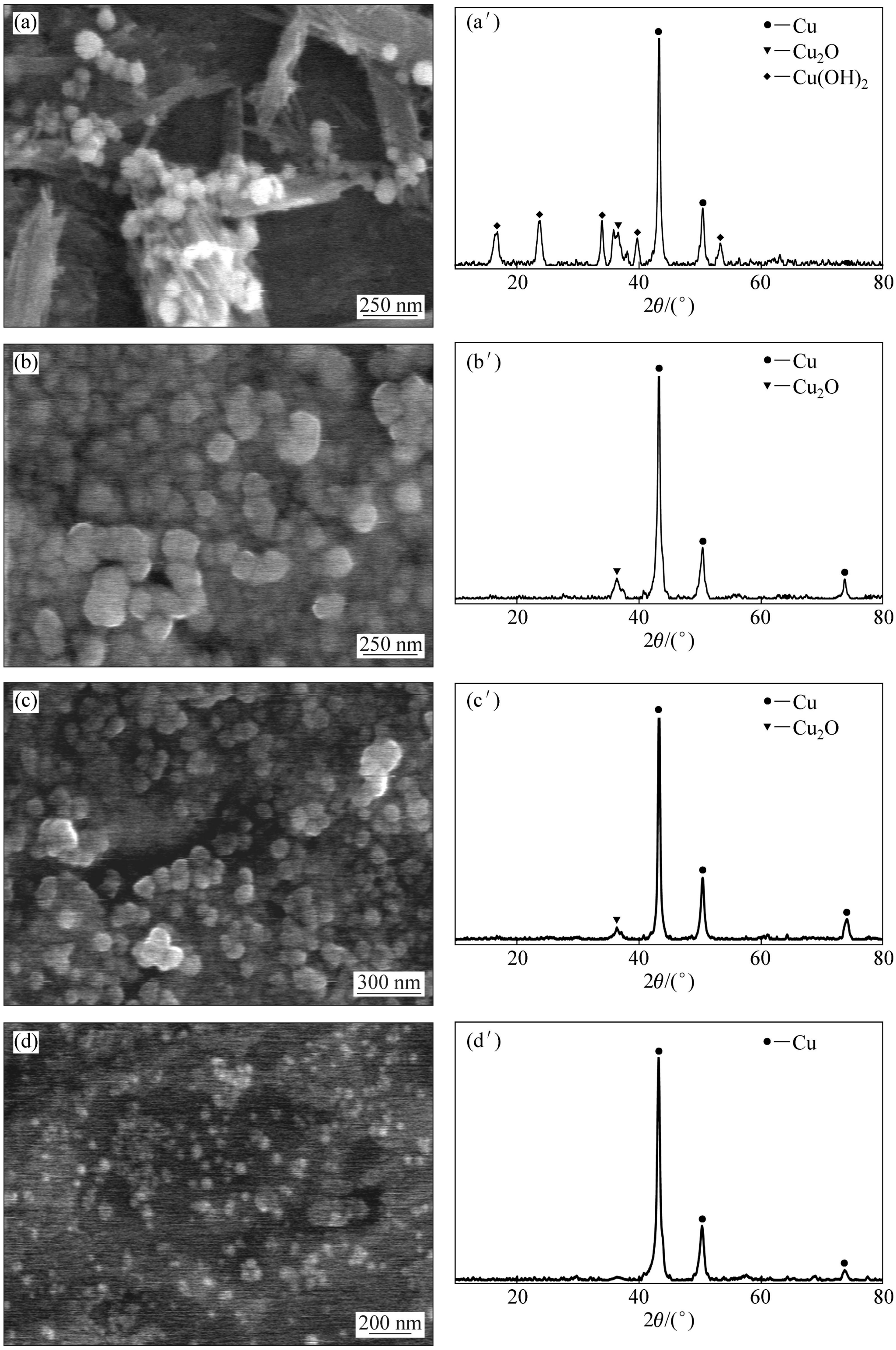


Fig. 2 SEM images and XRD patterns of copper particles obtained using $NaBH_4$ with different concentration: (a), (a′) 0.05 mol/L; (b), (b′) 0.1 mol/L; (c), (c′) 0.2 mol/L; (d), (d′) 0.4 mol/L

$$Cu^{2+} + 4NH_3 \cdot H_2O = Cu(NH_3)_4^{2+} + 4H_2O \quad (2)$$

$$4Cu(NH_3)_4^{2+} + BH_4^- + 8OH^- = 4Cu + B(OH)_4^- + 16NH_3 + 4H_2O \quad (3)$$

When $KNaC_4H_4O_6$ is adopted as complexant,

$$Cu^{2+} + 2C_4H_4O_2^{2-} = Cu(C_4H_4O_6)_2^{2-} \quad (4)$$

$$4Cu(C_4H_4O_6)_2^{2-} + BH_4^- + 8OH^- = 4Cu + B(OH)_4^- + 8(C_4H_4O_6)_2^{2-} + 4H_2O \quad (5)$$

And when $C_6H_5O_7Na_3$ is adopted as complexant,

$$Cu^{2+} + 2C_6H_5O_7^{3-} = Cu(C_6H_5O_7)_2^{4-} \tag{6}$$

$$4Cu(C_6H_5O_7)_2^{4-} + BH_4^- + 8OH^- = 4Cu + B(OH)_4^- + 8C_6H_5O_7^{3-} + 4H_2O \tag{7}$$

With fixed values of 0.2 mol/L Cu^{2+}, 0.4 mol/L $NaBH_4$, 1% gelatin and pH of 12, the effect of different complexants on Cu nanoparticles preparation was investigated. The results are shown in Fig. 4. With 1.2 mol/L $NH_3 \cdot H_2O$, 0.6 mol/L $KNaC_4H_4O_6$ and 0.6 mol/L

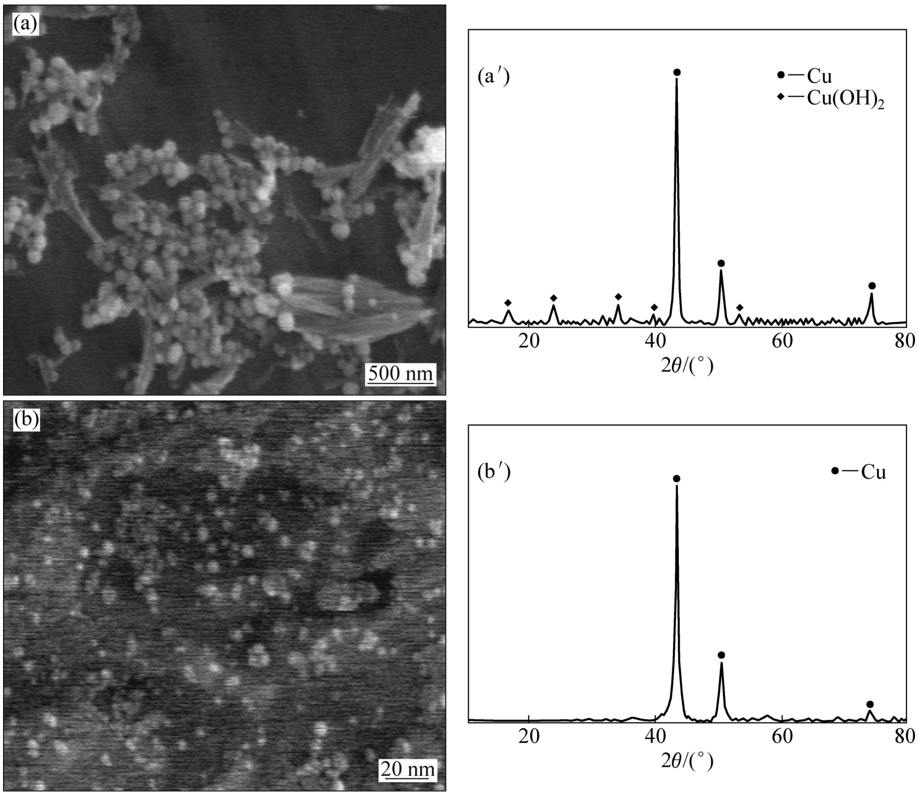


Fig. 3 SEM images and XRD patterns of copper particles obtained using $NaBH_4$ at different dripping rates: (a), (a′) 5 mL/min; (b), (b′) 50 mL/min

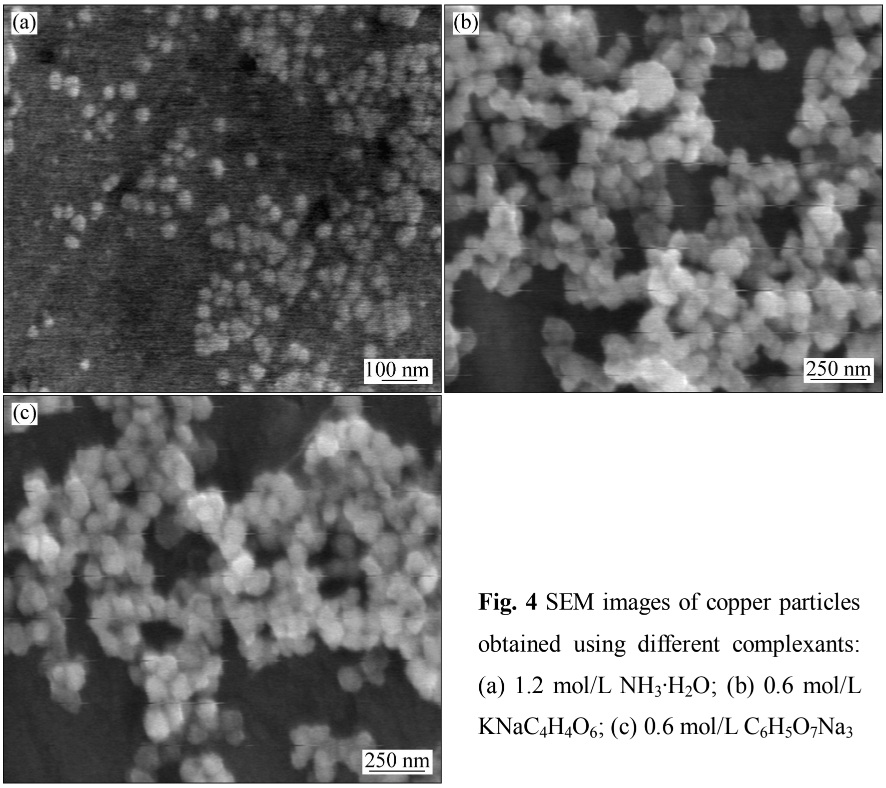


Fig. 4 SEM images of copper particles obtained using different complexants: (a) 1.2 mol/L $NH_3 \cdot H_2O$; (b) 0.6 mol/L $KNaC_4H_4O_6$; (c) 0.6 mol/L $C_6H_5O_7Na_3$

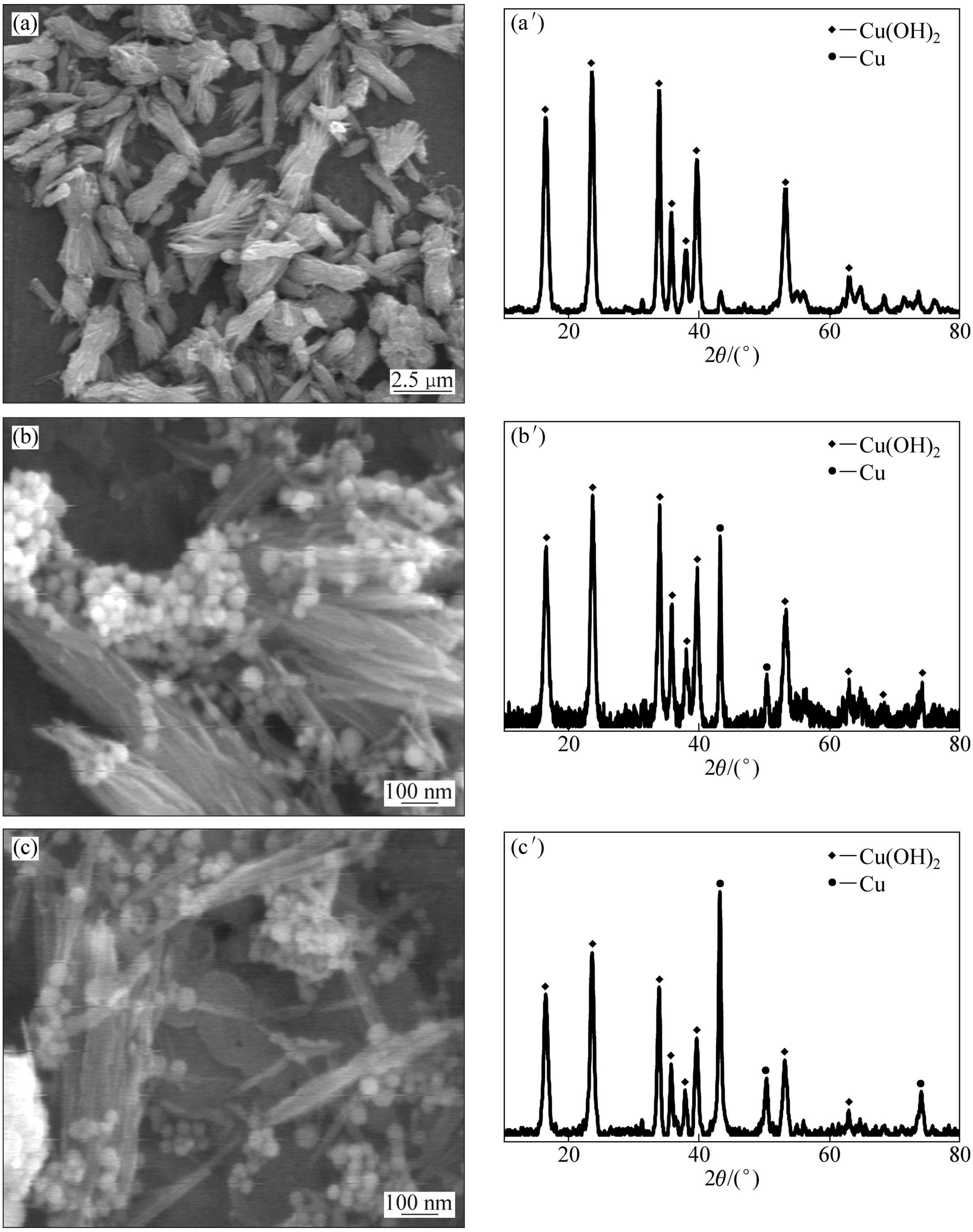
$C_6H_5O_7Na_3$ as the complexants, the average sizes of Cu particles obtained are 42, 115 and 108 nm, respectively. Thus, $NH_3{\cdot}H_2O$ is the optimal complexant for precursor formation.

3.4 Reduction process at different reaction time

A series experiments were conducted to study the reactions occurring during Cu nanoparticles formation. At fixed values of 0.2 mol/L Cu^{2+}, 0.4 mol/L $NaBH_4$, 1% gelatin and pH=12, the size distribution, SEM images and XRD patterns of the Cu nanoparticles at different reaction time points (0, 0.5, 1, 3, 5, 10 and 60 min) were examined. The results are shown in Fig. 5. The SEM images and XRD patterns show that during the initial stages of the reaction, the majority of the particles is rod-shaped $Cu(OH)_2$. Within 5 min, $Cu(OH)_2$ disappeared. The XRD patterns at 10 and 60 min are similar to that obtained at 5 min, indicating the completion of the reduction reaction within 5 min. The XRD patterns also show that all the Cu^{2+} ions are transformed to $Cu(OH)_2$ before the two solutions are mixed. $Cu(OH)_2$ is then reduced to Cu nanoparticles by $NaBH_4$. The final reaction process can be represented as

$$Cu^{2+}+2OH^{-}=Cu(OH)_2 \tag{8}$$

$$4Cu(OH)_2+BH_4^{-}=4Cu+B(OH)_4^{-}+4H_2O \tag{9}$$



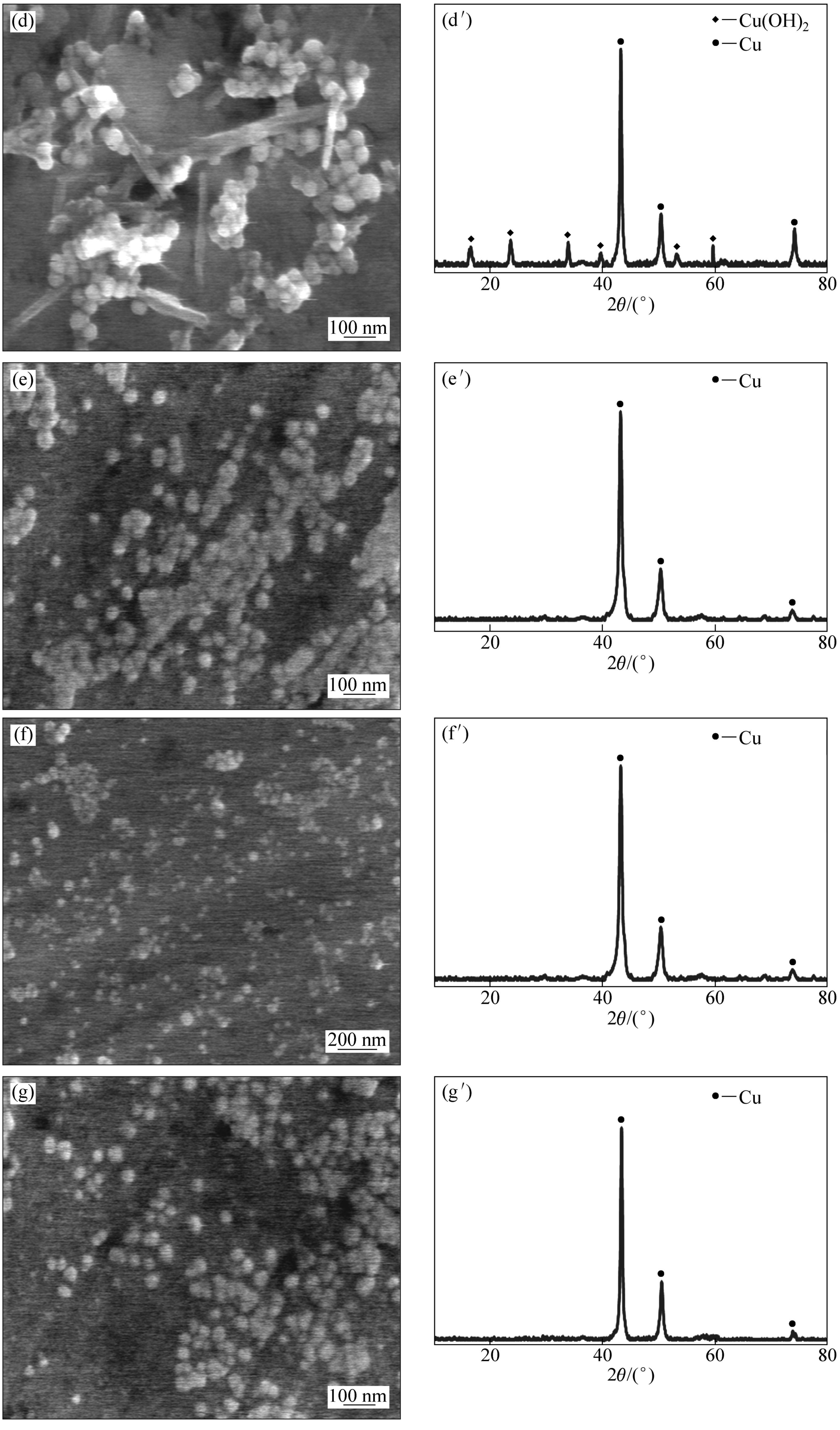


Fig. 5 SEM images and XRD patterns of copper particles obtained at different time points: (a), (a′) Before mixing; (b), (b′) After 0.5 min; (c), (c′) After 1 min; (d), (d′) After 3 min; (e), (e′) After 5 min; (f), (f′) After 10 min; (g), (g′) After 60 min

4 Conclusions

1) The average size of the Cu nanoparticles reduces with increasing excess of $NaBH_4$ to Cu^{2+}. When the Cu^{2+} and $NaBH_4$ concentration are 0.2 and 0.4 mol/L, the dripping rate is 50 mL/min, gelatin concentration is 1%, pH=12 and solution temperature is 313 K, the finest Cu nanoparticles (37 nm) are obtained.

2) Among $NH_3 \cdot H_2O$, $KNaC_4H_4O_6$ and $C_6H_5O_7Na_3$, the optimal complexant is found to be $NH_3 \cdot H_2O$ for precursor formation. The smallest Cu nanoparticles are obtained with 1.2 mol/L $NH_3 \cdot H_2O$.

3) During the reaction process, Cu^{2+} is transformed to $Cu(OH)_2$ before combination of the solutions and then this $Cu(OH)_2$ is reduced by the addition of $NaBH_4$ solution.

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$NaBH_4$的水性还原法制备纳米铜颗粒

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摘 要：在碱性溶液中用 $NaBH_4$ 还原 Cu^{2+}制备纳米铜颗粒，研究 $NaBH_4$ 浓度和滴加速率对 Cu 纳米颗粒制备的影响。反应的最佳条件是：0.2 mol/L Cu^{2+}，溶液 pH 12，温度 313 K，1%明胶作为分散剂，将 0.4 mol/L $NaBH_4$ 溶液以 50 mL /min 的速率加入 $CuSO_4$ 溶液中。氨水是最佳的络合剂。采用一系列实验研究不同时间点的反应进程。

关键词：纳米铜颗粒；水性还原法；前驱体；反应进程

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