

Direct reduction of copper oxide into copper under hydrothermal conditions

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Abstract A new preparation method of Cu from CuO under hydrothermal conditions was investigated. Glucose was employed as reducing agent. Results showed that CuO can be reduced easily to Cu⁰ with glucose as reductant at 220–250 °C with NaOH. The reaction conditions such as reaction time, reaction temperature, sodium hydroxide concentration and water filling played key roles in the purity of the products. The proposed method provides an efficient and green conversion of CuO into Cu⁰ without an expensive and toxic reducing agent at low temperatures.

Keywords Copper oxide · Reduction · Hydrothermal · Glucose

Introduction

Copper is an important metal material and has wide applications in many fields. We rely on copper for power, lighting, heating, communications, water supply and transport. It is hard to imagine a world without copper. Copper existing in nature is mainly in the form of ores containing oxygen or sulfur. In traditional methods, copper can be produced either pyrometallurgically or hydrometallurgically. The former route requires large amounts of energy and produces furnace gases with low sulfur dioxide concentrations. The latter process relies heavily on sulfuric acid as leaching agent, organic solvents as extractant, and using toxic reductant (e.g., ammonia, heavy oil, petroleum gas) [1, 2]. Neither are environment-friendly in the view of green chemistry. Thus, the development of a green and practical method of producing Cu from CuO is strongly desired.

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It is well known that water is an environmentally benign solvent. Recently, hydrothermal reactions have become a powerful tool for the conversion of biomass into value-added products [3–6]. High temperature water behaving as a reaction medium has outstanding properties in density, dielectric constants, ion product, viscosity, diffusivity, electric conductance and solvent ability [7]. Therefore, the hydrothermal process is one of the most promising methods for green production of copper.

Biomass is commonly recognized as one of the most important renewable resources. In our previous work, conversions of biomass into chemicals such as lactic acid, formic acid and acetic acid were studied [8–13]. Results indicated that some metal compounds could be reduced by biomass under hydrothermal conditions. Herein, we report a facile and green method toward the conversion of copper oxide into copper. It is the first report to the best of our knowledge on the formation of copper from copper oxide by using glucose (a model compound of carbohydrate biomass) as a reductant at low temperature. The effects of reaction time, reaction temperature, sodium hydroxide concentration, molar ratio of reactants and water filling on the conversion of copper oxide into copper, and its possible formation process, were investigated.

Experimental

All reagents were purchased from Sinopharm Chemical Reagent, (China), and used as received (analytical purity $\geq 99\%$) without further purification. In a typical procedure, 1.802 g (10 mmol) β -D-glucose was dissolved in 15 mL distilled water. Subsequently, 10 mL of 1 M NaOH solution and 0.4773 g (6 mmol) CuO were added, respectively. The mixture was stirred with a magnetic blender for some minutes and was transferred into a Teflon-line stainless-steel autoclave (50 mL) and heated at 250 °C for 3 h. Then, the system was allowed to cool naturally to room temperature. A brick red product was collected, washed with distilled water and absolute ethanol several times to move impurities, and dried in vacuum at 40 °C for 4 h.

The phase purity of the products was determined by X-ray diffraction (XRD) using Bruker D8 Advance X-Ray Diffractometer equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), employing a scanning rate of $0.02^\circ \text{ s}^{-1}$ and 2θ ranges from 20° to 80° . The accelerating voltage was set at 40 kV with a 40-mA flux. Diffraction patterns were compared with reference data in the ICDD PDF-2 database. The quantity analysis of compositions of products was performed by TOPAS [14]. HPLC analysis was performed with a HPLC system (Agilent 1200) equipped with a UV/VIS detector. Two Shodex KC811 columns were used in series. The solvent was 2 mM of HClO₄ with a flow rate of 1.0 mL min^{-1} . Peak identification was accomplished by the comparison of sample peak retention times with those of standard solutions of pure compounds. Particle size distribution was measured by a laser retardance technique using EyeTech Particle Size Analyzer with PD-10 Dry powder dispersion unit.

Results and discussion

The corresponding experimental conditions and compositions of samples are listed in Table 1. Figure 1a shows an XRD pattern of original CuO particles and all peaks belonging to it. The XRD pattern of Cu from sample S6 is presented in Fig. 1b. Three diffraction peaks centered at 43.3° , 50.5° and 74.2° can be clearly seen and were indexed as the (111), (200) and (220) planes of cubic Cu form by comparison with PDF-2 card files, No. 70-3039. No obvious XRD peaks arising from possible impurity phases such as CuO and Cu₂O were observed, indicating that the product was quite pure.

Usually, temperature is one of the most important factors to affect a chemical reaction. In this study, experiments were carried out at a temperature range of 110–250 °C (S1–S6). High yield Cu particles were obtained in 3 h at 250 °C (Fig. 1). When the temperature was decreased to 220 °C, pure Cu particles were also formed only prolonging the reaction time to 6 h (Fig. 2b). However, when the sample was heated for 10 h at 180 °C under keeping other conditions constants, the products were no longer pure Cu. The XRD pattern (Fig. 2c) of the obtained sample showed that the sample was some Cu₂O crystallized along with Cu. On continuing to decrease the reaction temperature to 110 °C, there were Cu, Cu₂O and CuO in products according to the XRD pattern analysis. The above results indicate that the

Table 1 The corresponding experimental conditions and composition of samples

| Sample | Glucose (mmol) | CuO (mmol) | NaOH (mmol) | Water filling (%) | Temperature (°C) | Time (h) | Figure | Products (%) |
|--------|----------------|------------|-------------|-------------------|------------------|----------|---------|---|
| S1 | 10 | 6 | 10 | 50 | 110 | 12 | Fig. 2d | CuO (41.0), Cu ₂ O (56.07), Cu (2.91) |
| S2 | 10 | 6 | 10 | 50 | 180 | 10 | Fig. 2c | Cu ₂ O (14.95), Cu (85.05) |
| S3 | 10 | 6 | 10 | 50 | 220 | 3 | – | Cu ₂ O (4.67), Cu (95.33) |
| S4 | 10 | 6 | 10 | 50 | 220 | 6 | Fig. 2b | Cu |
| S5 | 10 | 6 | 10 | 50 | 250 | 1.5 | – | CuO (2.59), Cu ₂ O (13.90), Cu (83.51) |
| S6 | 10 | 6 | 10 | 50 | 250 | 3 | Fig. 1 | Cu |
| S7 | 10 | 6 | 2.5 | 50 | 250 | 3 | Fig. 3a | Cu |
| S8 | 10 | 6 | No | 50 | 250 | 3 | Fig. 3b | Cu ₂ O (6.99), Cu (93.01) |
| S9 | 10 | 6 | 2.5 | 50 | 220 | 6 | – | Cu |
| S10 | 10 | 6 | No | 50 | 220 | 6 | – | Cu ₂ O (7.81), Cu (92.19) |
| S11 | 5 | 6 | 10 | 50 | 250 | 3 | – | Cu |
| S12 | 5 | 6 | 2.5 | 50 | 250 | 6 | Fig. 4b | Cu ₂ O (2.11), Cu (97.89) |
| S13 | 10 | 6 | 10 | 0 | 250 | 1.5 | – | Cu |
| S14 | 10 | 6 | 10 | 0 | 220 | 3 | – | Cu |

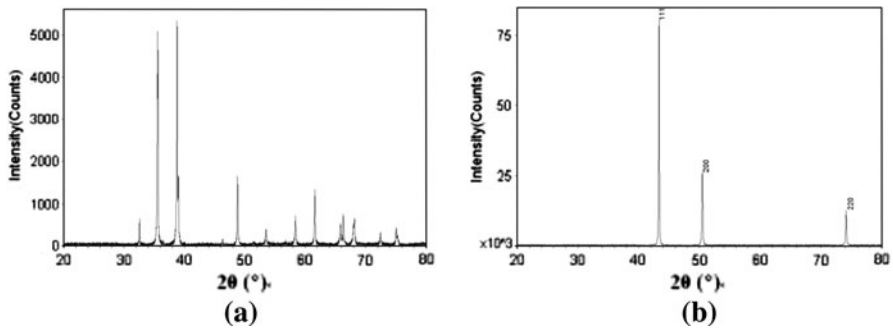


Fig. 1 XRD patterns of original CuO (a) and product Cu (b) particles

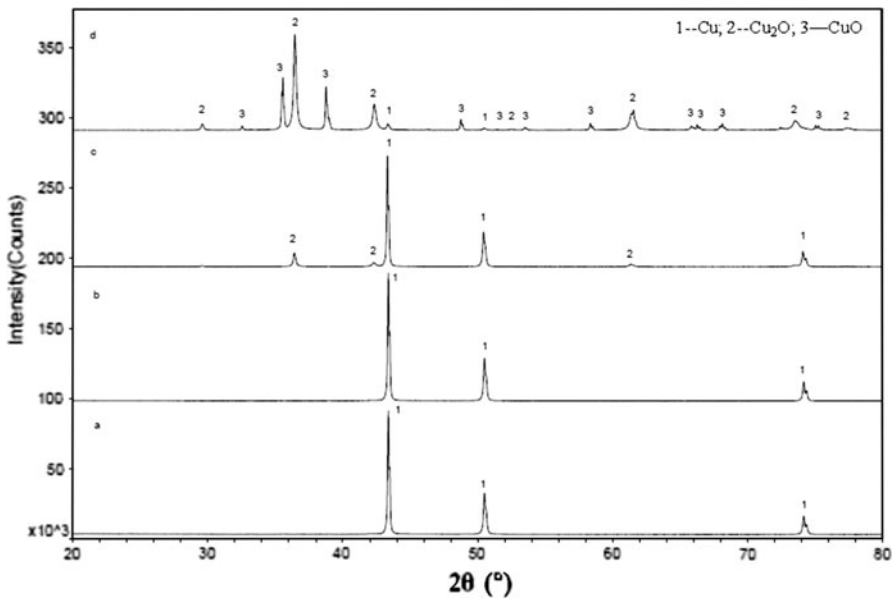


Fig. 2 XRD patterns of samples obtained at temperature 250, 220, 180, 110 °C, respectively: (a) S6, (b) S4, (c) S2, (d) S1

reducing power of glucose is stronger with increasing temperature so that elemental Cu appears. Similarly, when the temperature is lower, it is hard to reduce Cu (II) ions to Cu atoms completely.

Subsequently, the effect of NaOH supply on Cu production was examined at 250 and 220 °C (S7–S10). As shown in Fig. 3, the phase compositions of product were Cu and Cu₂O in the absence of NaOH when the sample was heated for 3 h at 250 °C, whereas the product was pure Cu in the same condition with NaOH of 0.4 or 0.1 M. The results were similar when the experiments were carried out at 220 °C.

Another factor influencing the composition of products is the molar ratio of reactants (glucose to CuO) in this system (S11, S12). When the samples were heated

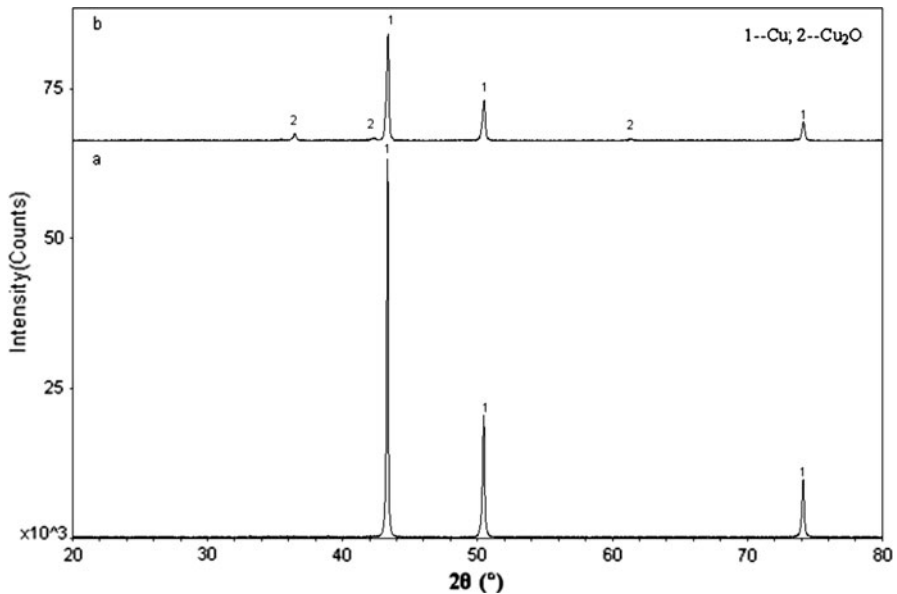


Fig. 3 XRD patterns of samples obtained with different NaOH concentration: (a) S7 (0.1 M NaOH), (b) S8 (without NaOH)

at 250 °C for 3 h with the molar ratio of glucose to CuO of 10/6 and NaOH of 0.4 or 0.1 M, pure Cu particles were obtained. However, if the molar ratio of glucose to CuO was adjusted to 5/6, Cu and Cu₂O were obtained when the NaOH concentration was 0.1 M, even prolonging the reaction time to 6 h. If the NaOH concentration was adjusted to 0.4 M, the sample consisted of pure Cu (Fig. 4).

Furthermore, we also investigated the influence of the water filling on the formation of the Cu at 250 and 220 °C (S13, S14), respectively. It was interesting that Cu particles were obtained rapidly without water. When the experiments were carried out with molar ratio of glucose to CuO of 5/3 in the presence of NaOH at 250 °C, only Cu crystals were obtained in 1.5 h. If the reaction temperature was adjusted to 220 °C and other conditions were kept constant, Cu crystals were obtained in 3 h. Compared to experiments with 50% water filling, the rate of reaction without water supply can be faster. The problem of the reaction without water filling is that the carbonization of glucose is serious. It is also difficult to separate Cu from carbon powder using simple physical methods.

In order to investigate the changes of particle size, the original CuO and Cu obtained under hydrothermal condition (S7) particle size distributions were analysed by laser particle size analyzer. As shown in Fig. 5, the average particle size of CuO and Cu is 6.19 μm (SD = 3.50 μm) and 1.46 μm (SD = 1.03 μm), respectively. The range of Cu particle size distribution is narrower than that of CuO.

In previous literature, glucose served as reducing agent to reduce Au(III) to the ground state rapidly at ambient temperature and itself converted to gluconate [15]. In this study, when the experiments were carried out with the molar ratios of glucose

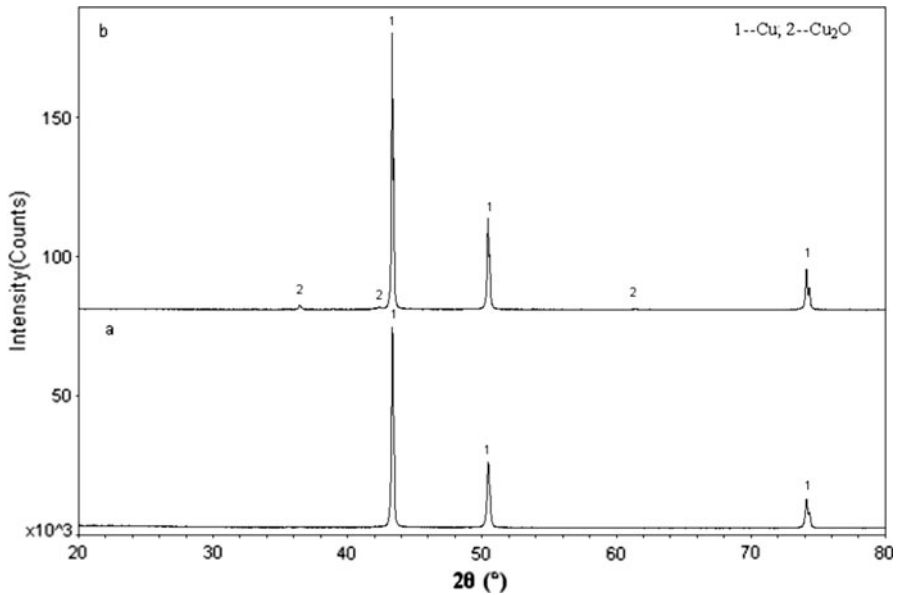


Fig. 4 XRD patterns of samples with different molar ratios of reactants (glucose to CuO) in 0.1 M NaOH: (a) S7 (10/6), (b) S12 (5/6)

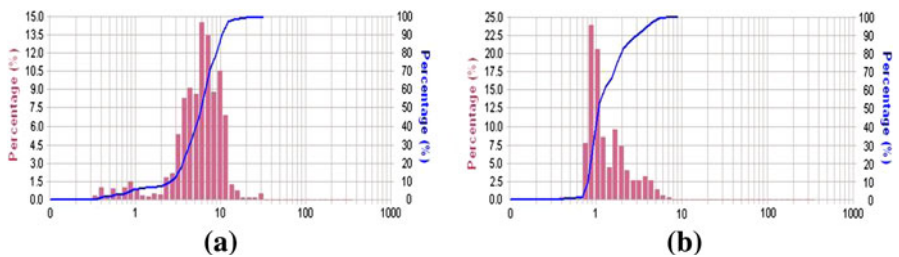


Fig. 5 The particle size distributions of CuO (a) and Cu (b)

to CuO of 5/6 at definite conditions, pure Cu were obtained. This indicates that reaction mechanism is different from that of the literature. If 1 mol glucose fully converted to 1 mol gluconate, 2 mol electrons would be transferred to oxidant, that is, only 1 mol CuO can be reduced. In fact, we found lactic acid, formic acid and other organic acids existed in liquid samples after the reactions (Fig. 6). On the basis of the theoretical and experimental results, the mechanism of Cu formation can be proposed. Glucose is a kind of polyol and can react with Cu^{2+} ions to form a stable complex [16], and thereby can enhance the solubility of CuO. With the increase of temperature and aggression of sodium hydroxide, the stability of the complex decreased. The electrons of hydroxyl oxygen atom in glucose transferred to Cu ions. The redox reaction took place. Cu particles were obtained and glucose was decomposed to small molecule substance such as lactic and formic acid. Based on the above consideration, the possible process can be expressed as follows:

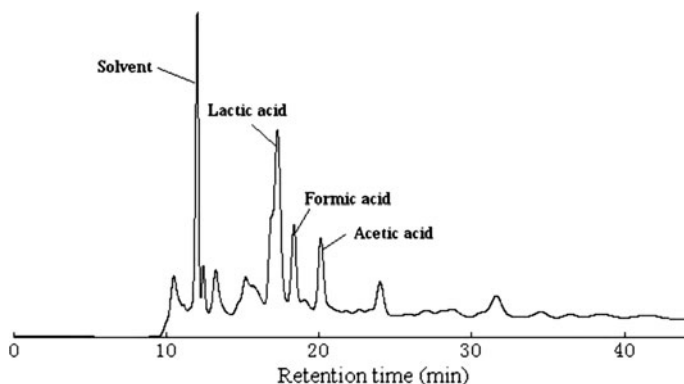


Fig. 6 HPLC chromatograms for liquid sample of S6



Further investigations will enable us to elucidate the reaction mechanism and lead to precise control over the size of Cu particles.

Conclusions

An easy hydrothermal route has been adopted to produce Cu from CuO, which made use of glucose in the presence of NaOH at a temperature range of 110–250 °C for 1.5–12 h in an autoclave. The reaction conditions such as reaction time, reaction temperature, sodium hydroxide concentration and water filling played important roles in the composition of the products. Pure metallic Cu which mean particle sizes are 1.46 μm can be obtained at the reaction with molar ratio of glucose to CuO of 10/6 and 0.1 M NaOH supply at 250 °C. The proposed method provides an efficient and green conversion of CuO into Cu without an expensive and toxic reducing agent at low temperature.

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