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Mechanochemical Synthesis of Ultrafine Cuprous Oxide Using Glucose as Reducing Agent

YongChol Kim, ChungIl Kim, JongGuk Kim

Faculty of Chemical Engineering, Kim Chaek University of Technology, Pyongyang 950003, Democratic People's Republic of Korea

Abstract- Cuprous oxide is used as an antimicrobial and fungicide of fruit trees and is widely used as a catalyst for photodegradation of organic contaminants in the visible light region. Cuprous cuprous oxide was successfully prepared by simple mechanochemical method at any place by varying the amount of reactants added in the system consisting of copper sulphate, sodium hydroxide and glucose without any heat source or complex device, the mode of addition of reactants, the grinding time and the aging conditions of the product. First, CuSO4·5H2O and NaOH were ground to a size of about 100 μm, respectively. Then, the ground copper sulfate was homogeneously mixed with glucose powder, a reducing agent and dodecyl sodium sulfate (SDS), a dispersing stabilizer. It was then mixed with a suitable amount of the ground NaOH and underwent a simple mechanochemical method of ball milling with an agate mortar to prepare ultrafine cuprous oxide in solid phase consisting of copper sulfate, sodium hydroxide and glucose. The results show that ultrafine cuprous oxide was obtained after 30 min of ball-milling without combustion of glucose as reducing agent when adding NaOH twice. The as-prepared ultrafine cuprous oxide was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) and it correspond to a cubic structure with size of 30-40 nm.

Keywords- Cuprous oxide; Mechanochemical method; Ball milling; Copper sulfate; Glucose.

I. INTRODUCTION

Cuprous oxide has good antibacterial and photocatalytic properties in the visible range, so there is currently an active research on the use of cuprous oxide as a disinfectant and antimicrobial agent. Cuprous oxide is a typical p-type semiconductor with a band gap of 2.0-2.2 eV. With its excellent photoelectric, optical and catalytic properties, it has been widely used in the fields of electrode materials for solar energy conversion [1], sensors [2], photocatalysts [3-5], fungicides and antibacterial agents [6-9]. It is widely used as a pigment for paints, glass and ceramics in the inorganic chemical industry [10] and it also finds its use as a disinfectant for fruit trees in agriculture [6], and as a poison for the preparation of waterproof coatings to prevent the attachment of marine organisms such as mussels and scallops to ships and marine structures [11-13].

Many studies have addressed its preparation and application. Typical methods to prepare cuprous oxide include solid-phase reduction [14], wet chemical method [15-17], electrochemical method [18], hydrothermal synthesis [19] and irradiation [20]. Recently, the preparation of cuprous oxide by a mechanochemical method has been reported, which is simpler in process and less environmentally friendly avoiding the drawback of wet chemistry [3, 9, 10, 21, 22].

Nano-cuprous oxide with a size of 50 nm to 150 nm was prepared by a mechanochemical method in which Cu powder was milled in a ball mill for more than 6 h in a CuCl2 solution with different concentrations of Cl- [10]. Nano-cuprous oxide was prepared by calcination of the synthesized precursor by ball milling using Cu2(OH)2CO3 and H2C2O4•2H2O [3]. Cuprous oxide powder was obtained by adding different reducing agents to copper sulfate, copper chloride and copper nitrate as copper compounds and grinding them in a mortar[21]. Copper sulfate, sodium hypophosphite and dimethylsulfoxide were added to a mortar and then homogeneously stirred and ground at 10 °C for 50 min, followed by washing with deionized water, ethanol and acetone and drying to obtain

nano-cuprous oxide. copper chloride, sodium borohydride and dimethyl sulfoxide were added to a mortar and homogenized, ball-milled at 70 °C for 20 min, washed with deionized water, ethanol and acetone, and dried to obtain nano-cuprous oxide.
Meanwhile, copper sulfate, ascorbic acid and dimethyl sulfoxide were added to a mortar and homogenized, ball-milled at 40 oC for 20 min, washed with deionized water, ethanol and acetone, and dried to obtain nano-cuprous oxide. Copper nitrate, sodium sulfite and dimethyl sulfoxide were added to a mortar and homogenized, ball-milled at 50 oC for 30 min, washed with deionized water, ethanol and acetone, and dried to obtain nano-cuprous oxide. They proposed synthesis method of nano-cuprous oxide that copper acetate, triethanolamine, dimethylsulfoxide and a small amount of acetic acid were mixed homogeneously, ball milled and washed at 35 oC for 6 h, and dried. The preparation process of cuprous oxide from copper compounds uses copper sulfate, copper nitrate and copper acetate as copper compounds, and various reducing agents are used to produce the desired product. Typical reducing agents are sodium sulfite, hydrazine hydrate, sodium hypophosphite, sodium borohydride, ascorbic acid, glucose, etc. However, reducing agents such as sodium sulfite and hydrazine are toxic and have a harmful effect on the environment. Therefore, there has been a considerable amount of research on the preparation of cuprous oxide by wet method using glucose as a mild reducing agent. This method requires complex equipment, large amount of heat, is applied in mass production, and a large amount of waste must be disposed of. We required to prepare nano-cuprous oxide by mechanochemical method using glucose which is suitable for producing small amount of antibacterial agent in any place. But the mechanochemical process produce too much heat thus the reduction by glucose is not feasible.

In this paper, we investigate the effect of the addition of copper sulfate and NaOH, reaction time and aging condition of products on the preparation of ultrafine cuprous oxide by the mechanochemical method, and based on their analysis, we determine the method for the preparation of ultrafine cuprous oxide from the mixture of copper sulfate, sodium hydroxide and glucose.

II. EXPERIMENTAL

Materials

Copper sulfate pentahydrate (99.8%), sodium dodecyl sulfonate (SDS) and sodium hydroxide were purchased from Sigma Aldrich. Glucose used was of analytical grade.

Preparation method

To prepare ultrafine cuprous oxide, ball-milling was done in an agate mortar with pentahydrate of copper sulfate as precursor, glucose as reducing agent, sodium dodecyl sulfonate (SDS) as dispersant. The experimental procedure was as follows.

First, the required amounts of copper sulfate pentahydrate, sodium hydroxide and glucose were ground, respectively. Then, copper sulfate, glucose and SDS were mixed homogeneously and ball-milled in an agate mortar while adding the ground sodium hydroxide. As the milling time increased, the color of the mixture changed from light blue to orange. The reaction was carried out for 30 min.
The milled product was taken, dissolved in distilled water, stirred and then aged so that the layers be separated. After filtering and washing several times with distilled water and ethanol, it was dried at 60 oC for 4 h to obtain the powder. The as-prepared ultrafine cuprous oxides were characterized by XRD and SEM analysis.

III. RESULTS AND DISCUSSION

Thermodynamic analysis of the reaction process of copper hydroxide formation from copper sulfate
The maximum attainable temperature was calculated by "HSC Chemistry 9.0" program, assuming a closed system of reaction (Eq. 1) for the mechanochemical reaction of copper hydroxide from copper sulfate. The formation of copper oxide from copper sulfate is as follows:

$$CuSO4•5H2O+2NaOH→Cu(OH)2+Na2SO4+5H2O$$

(1) Reaction proceeds at 298.15 K, and the heat released by the system is considered to be adiabatically heated. The standard heat of formation data of the materials used in the calculations are shown in Table 1.

Table 1 Standard heat of formation of various materials

Material	Standard heat of formation $\Delta_f H^0_{298.15}$/kJ/mol
$CuSO_4 \cdot 5H_2O$	-2276.515
NaOH(s)	-425.800
$Cu(OH)_2$	-450.400
Na_2SO_4	-1387.900
H_2O	-285.830

The standard isobaric heat of the reaction at 298.15 K for reaction (1) was calculated from Eq. (2).

(2)

The calculations were carried out in the adiabatic closed-loop system, in which all substances in the reaction system were present in normal state, and the thermal effects outside the reaction heat inside the reaction system were neglected. Assuming the absolute value of the heat of reaction and the amount of heat required to heat the products equal, we can find the maximum temperature T3, which is the integral top of the following equation:

(3)

On the right-hand side of the above equation, is the sum of the isobaric molar heat capacity of the products.

(4)

Table 2 Temperature dependent function of molar heat capacity at constant pressure Material

Material	$C_P = a + b \cdot 10^{-3}T + c \cdot 10^5 T^{-2} + d \cdot 10^{-6}T^2, \mathrm{J/(mol \cdot K)}$			
	a	*b*	*c*	*d*
$Cu(OH)_2$	95.802	11.478	-18.869	0.027
Na_2SO_4	80.561	-159.545	0.058	-0.868
H_2O(l)	186.844	-464.247	-19.565	548.631

temperature is calculated from the calculated value of the temperature of the reaction system. It can be seen that the heat generated during the mechanochemical reaction can be used as the heat energy required for the reduction of cuprous oxide.

Considerations of the reduction process by glucose

The possibility of the direct formation of copper oxide from copper sulfate during ball milling of copper sulfate and sodium hydroxide using glucose as a reducing agent was examined. The reaction is as follows:

(5)

Since formal potential of reaction (5) is (>) [24], it is known that the above redox reaction proceeds. Thus, glucose can be used as a reducing agent.

Effect of addition of reactants

Glucose is used as a reducing agent to prepare cuprous oxide from copper sulfate (6):

2CuSO4+C6H12O6+5NaOH→Cu2O+C6H11O7Na+ 2Na2SO4+H2O (6)

The addition of reactants, addition mode, reaction time and aging condition on cuprous oxide preparation from copper sulfate and sodium hydroxide by the mechanochemical method with glucose as the reducing agent was investigated. The effect of NaOH and copper sulfate molar ratio (NaOH: copper sulfate) on the preparation of ultrafine cuprous oxide was evaluated. The reducing agent was glucose and ball-milling was done for 30 min adding NaOH twice, followed by 12 h of aging the product. The content of cuprous oxide was determined by titrating 0.02 M potassium permanganate solution with a platinum complex electrode in an automatic titrimeter DL 53 in the presence of hydrochloric acid (Fig. 1).

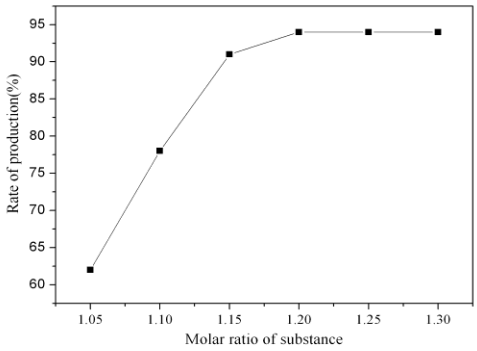

Fig. 1 Yield change of cuprous oxide with molar ratio change of sodium hydroxide and copper sulfate

As the adding amount of NaOH increases to 1.2 times the theoretical amount, the amount of Cu2O produced rapidly increases and then no significant change is observed for the further increase. It implies the 1.2 times is reasonable for the preparation of cuprous oxide.

Effect of reaction mixture mode

Product is influenced by addition modes of the reactants. In this work, Copper sulfate, sodium hydroxide and glucose were mixed homogeneously and ball-milled for 30 min in an agate mortar and 12 h of aging. If sodium hydroxide is added once to the mixture of copper sulfate, glucose and SDS, the reaction temperature increases rapidly hindering the glucose from acting as the reducing agent during combustion. It could be confirmed by that the mixture became black and then dark brown transforming into copper oxide. Hence, in our experiments, ball-milling was done adding NaOH twice to avoid an excessive temperature rise. Moreover, the addition mode was adjusted for the reaction temperature to not exceed 120 oC. Consequently, with milling time, the color of the reactant changed from blue to yellow and finally orange. It might be because that copper hydroxide produced in reaction (1) was reacted with glucose as a reducing agent by the heat generated through the mechanochemical process.

Effect of reaction time

When cuprous oxide is prepared by the mechanochemical method, the reaction time also affects the production rate of cuprous oxide. In the experiments, the desired amount of glucose and SDS dispersant were mixed uniformly and NaOH was added in two batches at a molar ratio of 1.2 of NaOH and CuSO4.

The effect of milling time on the preparation of ultrafine cuprous oxide by ageing the product for 12 h was investigated by X-ray diffraction analysis (XRD). The measurements of XRD were performed by a Bruker AXS D8 ADVANCE powder diffractometer with a CuKα1 characteristic line (λ=1.5406 Å) whose 2θ was shifted at a step interval of 0.02°/0.5 and controlled at 40 kV and 40 mA in the scanning range of 20° to 80°. The results are shown in Fig. 2.

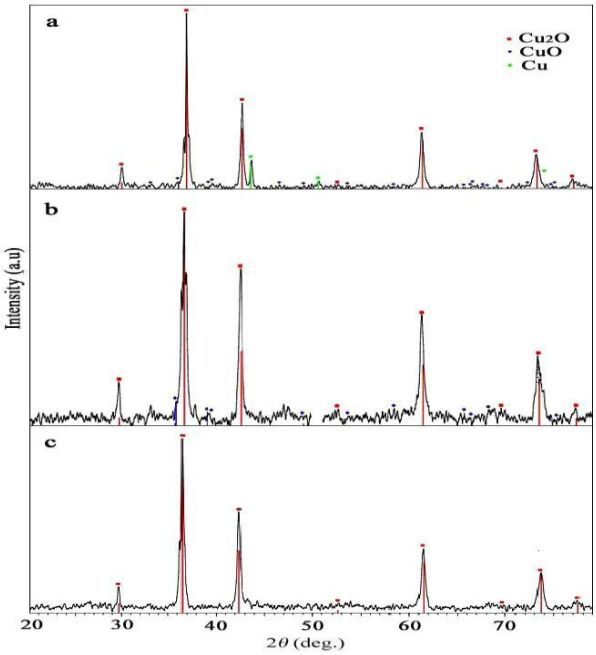

Fig. 2 XRD patterns with various milling time: a 15 min, b 20 min and c 30 min

When preparing ultrafine cuprous oxide from copper sulfate by mechanochemical method, as shown in Fig. 2, there is no reduced copper oxide with cuprous oxide at a shorter milling time.

When the milling time is over 30 min, all cupric ions of cupric oxide are reduced to cuprous oxide, and only the peak corresponding to cuprous oxide is observed in the diffraction peak. Hence, the appropriate grinding time for cuprous oxide preparation by mechanochemical method is 30 min.

Effect of aging condition of products

In the experiments, the effect of aging of the products after ball milling was investigated. The ageing effect was observed through the change in the percentage of cuprous oxide (XRD) with time after the product was dissolved in distilled water and homogeneously dispersed by stirring for a certain time. The reaction was carried out by adding a mixture of NaOH and CuSO4 of 1.2, ball milling time of 30 min and NaOH in two fractions. XRD of the products is shown in Fig. 3.

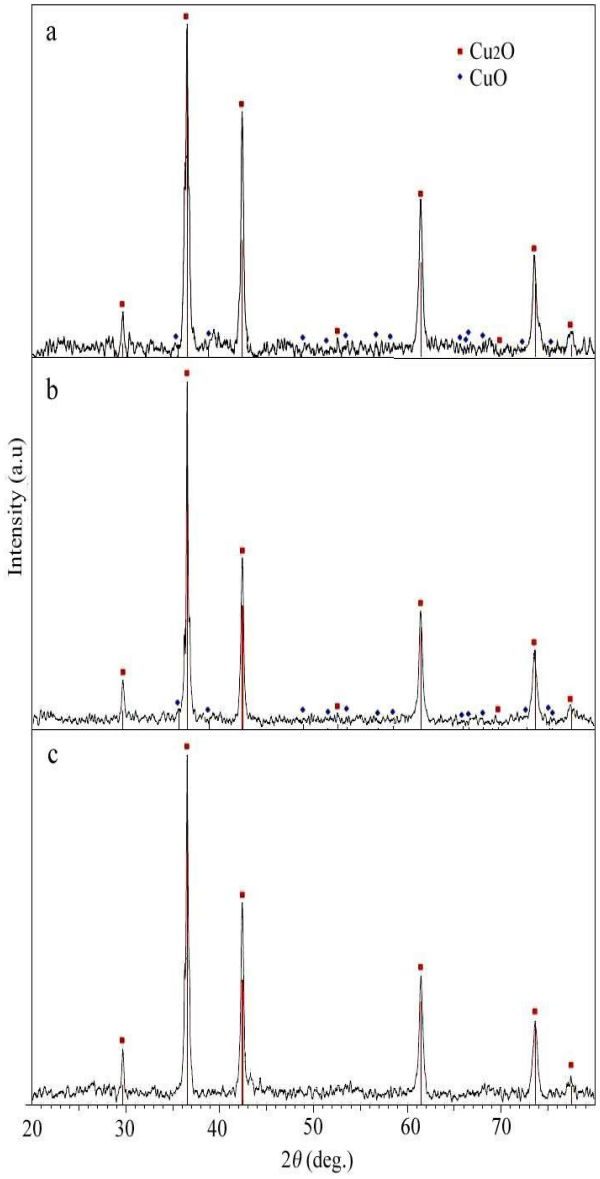

Fig 3 XRD patterns with various ageing time: a 6 h, b 9 h, c 12 h

XRD changes of ultrafine cuprous oxide with aging time. 12 h. As shown in Fig. 3, the reaction was completed at 12 h, and only the peak corresponding to cuprous oxide was observed in the X-ray diffraction pattern.

Considerations of the preparation of ultrafine cuprous oxide by mechanochemical methods

The preparation of ultrafine cuprous oxide by mechanochemical methods is accomplished by converting the reaction from a solid phase to a liquid phase. Copper sulfate with five crystal waters loses two crystal waters at 30 oC, becomes monohydrate at 110 oC, and anhydride at 250 oC, losing all crystal water [25].

Therefore, copper sulfate is formed by the loss of crystal water during ball milling, forming a thin layer of hydrated film on the surface of the particle, and sodium hydroxide is highly deliquescent, so that it is easily formed on the surface of the particle by atmospheric moisture.

At this time, the liquid phase reaction is easily carried out by the high heat of ball milling process because a layer of solution with a saturated concentration is formed on the particle surface of copper sulfate and sodium hydroxide. In addition, the formation of sodium sulfate crystals during the reaction, precipitation, and rapid increase in the system viscosity, inhibits the growth of the produced cuprous oxide particles, which are not fully-grown and are present in the fine fraction. From the above considerations, the suitable reaction conditions for the preparation of ultrafine cuprous oxide by mechanochemical method are as follows:

The addition of NaOH is 1.2 times the theoretical amount, the grinding time is 30 min, and the addition of NaOH in the reaction mixture and ball milling is not a single-step addition mode, but is reasonable to divide the addition into two stages. Products were aged for more than 12 h to obtain ultrafine cuprous oxide. The results of XRD (Bruker AXS•D8ADVANCE) and SEM (Scanning electron microscope, QUANTA-200, Holland) analysis of ultrafine cuprous oxide obtained are shown in Figs. 4 and 5. As shown in Figs. 4 and 5, the primary particles of the prepared ultrafine cuprous oxide are 36 nm in size, cubic in shape and well dispersed.

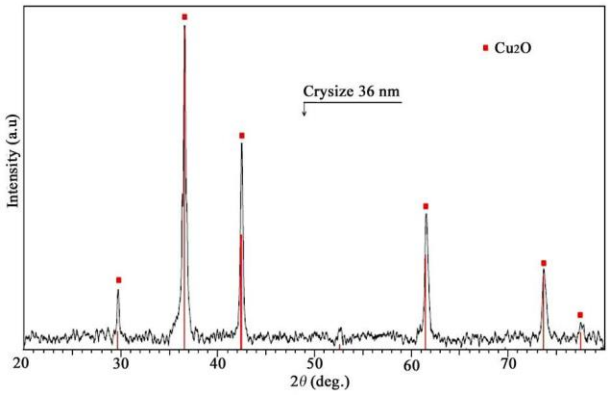

Fig. 4 XRD analysis of cuprous oxide prepared by mechanochemical method

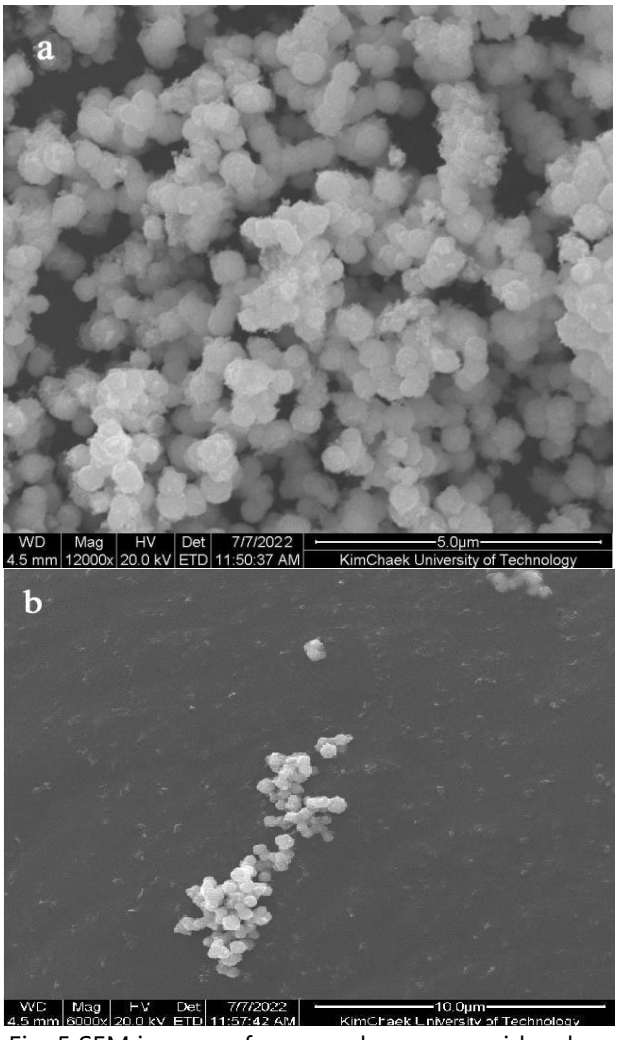

Fig. 5 SEM images of prepared cuprous oxide a low and b high resolution

IV. CONCLUSION

The effects of NaOH addition, reaction time, reaction mode of reactants and aging time of products on the preparation of cuprous oxide by mechanochemical method were investigated and it was found that ultrafine cuprous oxide could be prepared. The addition of SDS as dispersant, addition of NaOH in two steps followed by addition of NaOH before milling at 1.2 theoretical dose, 30 min milling time, and 12 h aging, resulted in cubic cuprous oxide with a primary particle size of 36 nm and good dispersion.

This approach does not require a large number of complex mechanical devices or equipment, and therefore can be easily applied to the preparation of ultrafine cuprous oxide at any site.

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Compliance with ethical standards
Conflict of interest The authors declare that there is no confict of interest.

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