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Preparation of Cu_2O nanoparticles in cupric chloride solutions with a simple mechanochemical approach

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ABSTRACT

The cuprous oxide (Cu_2O) nanoparticles with diameter of 50–150 nm are prepared by high-energy ball milling in the various $CuCl_2$ solutions with different $[Cl^-]$ concentration. The as-synthesized products are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). Finally, the effects of $[Cl^-]$ concentrations on the formation of cuprous oxide and reaction mechanism are discussed.

1. Introduction

The cuprous oxide (Cu_2O) nanoparticles are widely used as the antiseptic for shipping paint, the germicide in agriculture, the catalyzer in organic industries as well as the colorant stain for red glass and red enamel [1,2]. In recent years, it is particularly applied as the photocatalyst for overall water splitting under visible light irradiation, photo electron transition material and cathode material of lithium ion cell [3–5]. Thus, more and more research interest has been paid to the preparation and application of the Cu_2O nanoparticles.

Various preparation methods of Cu_2O nanoparticles have been developed, including electrolysis [6,7], thermal oxidation [8], hydrothermal production [9], reduction of cupric salts [10,11] or copper oxide [12] in solution and γ-irradiation method [13]. According to pH-Potential diagram of copper, Cu_2O is generally available in the neutral or alkali solutions [14]. However, it can also be obtained from the acid solutions reported by recent studies [15,16]. For instance, Jayewardena et al. obtained a layer of cuprous oxide film on the Cu plate by immersing the Cu plate in the HCl solution of pH 3 and stirring at 40 °C [15]. Diaminoethane and hexadecylamine were used as the buffering reagents for controlling the pH and the concentration of free Cu ions in the solution, which played an important role to prevent Cu^+ from being deoxidized to Cu [16].

Most recently, Cu_2O nanoparticles were successfully synthesized by milling Cu powders in acid solution (pH 2) in our previous work [17]. In this paper, Cu_2O nanoparticles with diameter of 50–150 nm were obtained in various concentration cupric chloride ($CuCl_2$) solutions by a simple mechanochemistry approach.

2. Experimental

The pure Cu powders are ground in chloride solutions by a planetary ball mill. Elemental Cu powders (5 g, 99.99%,–100 meshes) are selected as the raw material. Ball milling is carried out at 400 rpm in the Cu container containing 100 ml $CuCl_2$ solution with different $[Cl^-]$ concentration. The Cu balls with diameter of 15 mm are used and the weight ratio of balls to powders is 20:1. The as-milled products are washed by distilled water and then dried in vacuum at 40 °C for 2 h.

The as-milled powders are examined by X-ray diffraction (XRD) using Cu-Kα radiation in a Siemens D5000 X-ray diffractometer. The morphology of nanoparticles is characterized by JSM-6700F field emission scanning electron microscope (FESEM) and JEM-3010 high-resolution transmission electron microscope (HRTEM). The pH values of the solution were confirmed by Thermo PH510 meter. All the above procedures are conducted at room temperature.

3. Results and discussion

The as-milled products by milling Cu powders in various $CuCl_2$ solutions with different $[Cl^-]$ concentrations are shown in Table 1. From this table, Cu_2O single phase were obtained during 25–100 h for various $CuCl_2$ solutions. Figs. 1 and 2 illustrate the XRD patterns of the as-milled products in the $CuCl_2$ solutions at different

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Table 1
The as-milled products by milling Cu powders in various $CuCl_2$ solutions with different $[Cl^-]$ concentrations.

Milling time (h)	Phase constituents of the as-milled products (mass%)			
	0.3 mol $[Cl^-]$ (L)	7.5×10^{-2} mol $[Cl^-]$ (L)	1.5×10^{-2} mol $[Cl^-]$ (L)	0.75×10^{-2} mol $[Cl^-]$ (L)
3	Cu(26.5), CuCl(28.6), $Cu_2(OH)_3Cl$(36.4), Cu_2O(8.5)	Cu(90), CuCl(7.5), $Cu_2(OH)_3Cl$(0), Cu_2O(2.5)	Cu(60), CuCl(0), $Cu_2(OH)_3Cl$(19), Cu_2O(21)	Cu(60), Cu_2O(40)
6	Cu(8), CuCl(26.5) $Cu_2(OH)_3Cl$(42.5) Cu_2O(23)	Cu(45), CuCl(3.5), $Cu_2(OH)_3Cl$(21), Cu_2O(30.5)	Cu(23.7), CuCl(0), $Cu_2(OH)_3Cl$(13.5), Cu_2O(62.8)	Cu(66), Cu_2O(44)
10	Cu(8) CuCl(17.5) $Cu_2(OH)_3Cl$(51) Cu_2O(23.5)	Cu(12), CuCl(0), $Cu_2(OH)_3Cl$(43), Cu_2O(45)	Cu(8), CuCl(0), $Cu_2(OH)_3Cl$(8), Cu_2O(84)	Cu(50), Cu_2O(50)
25	Cu(5), CuCl(0) $Cu_2(OH)_3Cl$(49.5) Cu_2O(45.5)	Cu(0), CuCl(0), $Cu_2(OH)_3Cl$(35), Cu_2O(65)	Cu(0), CuCl(0), $Cu_2(OH)_3Cl$(0), Cu_2O(100)	Cu(0), Cu_2O(100)
50	Cu(0), CuCl(0) $Cu_2(OH)_3Cl$(48) Cu_2O(52)	Cu(0), CuCl(0), $Cu_2(OH)_3Cl$(24), Cu_2O(76)	–	–
80	Cu(0), CuCl(0) $Cu_2(OH)_3Cl$(30) Cu_2O(70)	Cu(0), CuCl(0), $Cu_2(OH)_3Cl$(0), Cu_2O(100)	–	–
100	Cu(0), CuCl(0) $Cu_2(OH)_3Cl$(0) Cu_2O(100)	–	–	–

milling time and the $[Cl^-]$ concentrations are 1.5×10^{-2} mol/L and 0.75×10^{-2} mol/L, respectively. SEM and TEM micrographs of Cu_2O particles obtained by this approach are showed in Fig. 3 and the $[Cl^-]$ concentration is 1.5×10^{-2} mol/L. The Cu_2O particles were about 50–150 nm in dimension and with cubic, hexagon and polygon shapes. Based on these results, it can be concluded that the milling time for obtaining single phase Cu_2O is shortened and the size of Cu_2O particles become finer and more regular with decreasing the $[Cl^-]$ concentration.

Although the exact mechanism and reaction route are not very clear yet, a series of reactions as follows are assumed during the whole process based on the present investigation results and previous research results [17]:

$$CuCl_2 + 2H_2O \rightarrow Cu(OH)_2 + 2HCl \quad (1)$$

$$CuCl_2 + Cu \rightarrow 2CuCl \quad (2)$$

$$Cu(OH)_2 + Cu \rightarrow 2CuOH \quad (3)$$

$$2CuOH \rightarrow Cu_2O + H_2O \quad (4)$$

$$CuCl_2 + 3Cu(OH)_2 \rightarrow 2Cu_2(OH)_3Cl \quad (5)$$

$$Cu(OH)_2 \rightarrow CuO + H_2O \quad (6)$$

$$CuO + Cu \rightarrow Cu_2O \quad (7)$$

The most essential reaction of all mentioned above is reaction (7), i.e., $CuO + Cu \rightarrow Cu_2O$ (or $Cu + Cu^{2+} \rightarrow 2Cu^+$). And it should be noted that the reaction (1) is generally limited and the $CuCl_2$ can not be hydrolyzed completely. Obviously, there are different

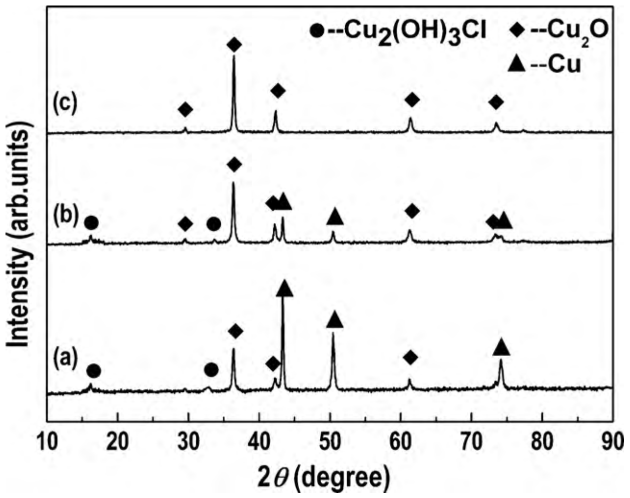

Fig. 1. XRD patterns of the products after 3 h, 6 h and 25 h milling Cu powders in the $CuCl_2$, which the $[Cl^-]$ concentrations are 1.5×10^{-2} mol/L.

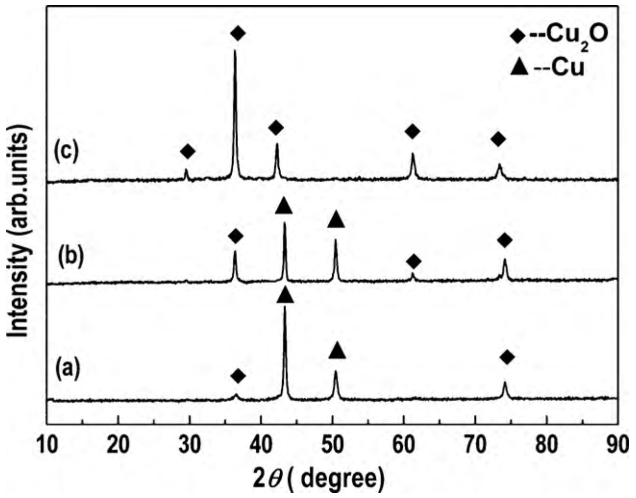

Fig. 2. XRD patterns of the products after 3 h, 6 h and 25 h milling Cu powders in the $CuCl_2$, which the $[Cl^-]$ concentrations are 0.75×10^{-2} mol/L.

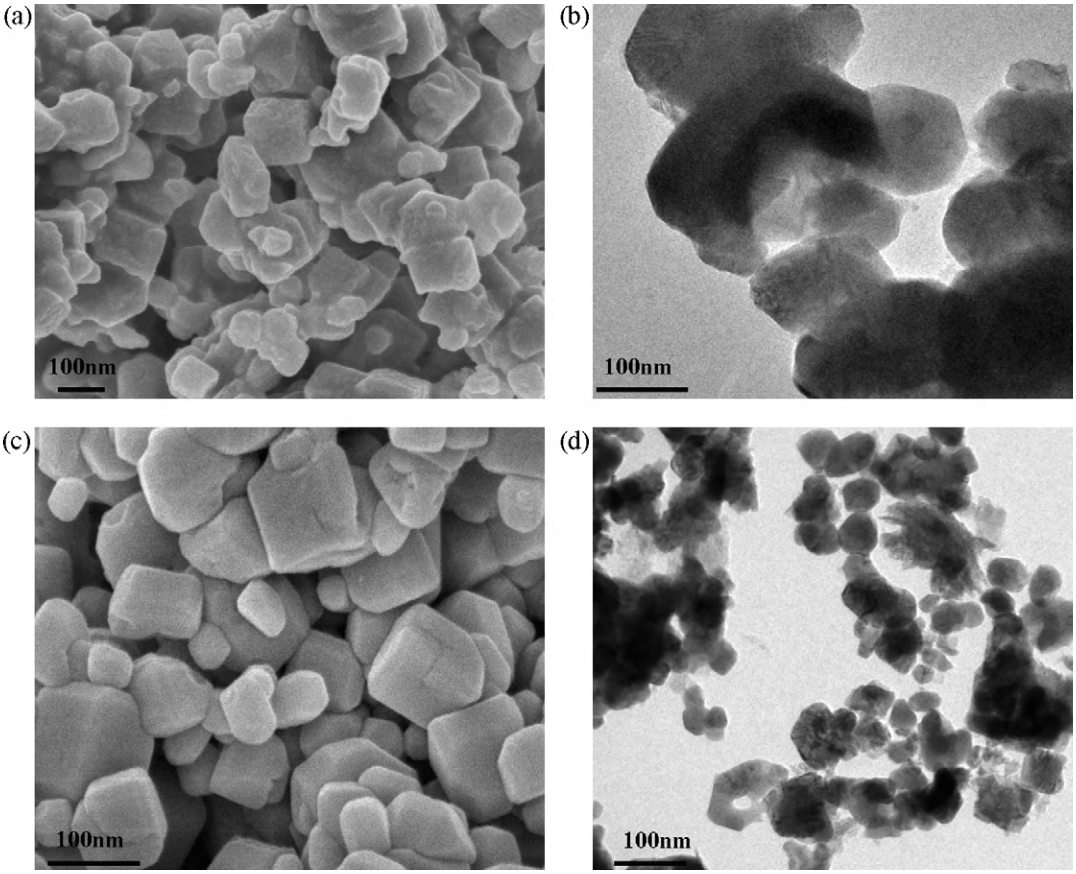

Fig. 3. SEM and TEM images of Cu_2O nanoparticles obtained by milling Cu powders in the $CuCl_2$ solution for 25 h which the $[Cl^-]$ concentrations are 0.75×10^{-2} mol/L (a, b) and 1.5×10^{-2} mol/L (c, d), respectively.

Table 2
PH values of various $CuCl_2$ solutions with different $[Cl^-]$ concentrations after different milling time.

Milling time (h)	pH values			
	0.3 mol $[Cl^-]$ (L)	7.5×10^{-2} mol $[Cl^-]$ (L)	1.5×10^{-2} mol $[Cl^-]$ (L)	0.75×10^{-2} mol $[Cl^-]$ (L)
0	3.5–4	4–4.5	5.5–6	6–6.5
3	3.5–4	4–4.5	5.5–6	6–6.5
6	4–4.5	4–4.5	5.5–6	6–6.5
10	4–4.5	5–5.5	5.5–6	6.5–7
25	4.5–5	5–5.5	5.5–6	6.5–7
50	4.5–5	5–5.5	–	–
80	4.5–5	5–5.5	–	–
100	5–5.5	–	–	–

reaction processes for various $CuCl_2$ solutions at different $[Cl^-]$ concentrations, which were proved by different products and relative content in the different milling time. Moreover, it should be noted that the reaction (5) may be very weak or even not to occur when the $[Cl^-]$ concentration is 0.75×10^{-2} mol/L because the $Cu_2(OH)_3Cl$ phase could not be found in the XRD patterns. Thus, it can be deduced that different $[Cl^-]$ concentration would affect reactions during different milling periods, e.g., the reaction time for forming single phase Cu_2O and the size as well as shape of Cu_2O nanoparticles.

Finally, this mechanochemistry approach can be considered as a kind of environment-friendly process with potential industrial application. Table 2 shows pH values of various $CuCl_2$ solutions with different $[Cl^-]$ concentrations after different milling time. It can be seen from this table that solutions will approach neutral after that the full Cu_2O nanoparticles are obtained. Furthermore, the $CuCl_2$ solution can be recycled and will not cause excess pollution to the environment.

4. Conclusions

1. The cuprous oxide nanoparticles with diameter of 50–150 nm are successfully synthesized by ball milling with copper powders in the $CuCl_2$ solution. Single phase Cu_2O is obtained at 25 h, 25 h, 80 h and 100 h for different $[Cl^-]$ concentrations of 0.75×10^{-2} mol/L, 1.5×10^{-2} mol/L, 7.5×10^{-2} mol/L and 0.3×10^{-2} mol/L, respectively.
2. It can be concluded that different concentration of $[Cl^-]$ would affect the reaction in different milling periods, e.g., time for forming single phase Cu_2O and size of Cu_2O nanoparticles.

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