Hydrothermal Synthesis of Rod-like Copper Oxide Crystals

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Abstract

A hyrdrothermal synthesis has been developd to prepare rod-like crystals of copper oxide using copper nitrate trihydrate as a function of synthesis temperature, stirring speed and solution pH value. The properties of the fabricated crystals were studied using scanning electron microscopy, X-ray diffraction and particle size analysis. The morphology of the synthesized CuO was dependent on both the pH value of the solution and the morphology of the seed materials. Synthesized particles have regular morphologies and a uniform size distribution.

Keywords : hydrothermal synthesis, copper oxide, rod-like crystals, copper nitrate trihydrate, morphology

1. Introduction

Copper oxide is a major industrial material and has been widely used for many applications, including gas sensors, catalysis, magnetic storage media, solar energy transformation and semiconductors [1-3]. A number of different of fabrication techniques have been reported for copper oxide. Among the various synthesis methods, the hydrothermal method is of interest because it is a reliable, controllable, and environmental-friendly synthesis procedure performed at moderate temperature [2]. It is well known that a hydrothermal method can be used to synthesize very fine crystals and control the morphology of the final product. With a decrease in particle size, fine particles may exhibit higher properties within the composites (e.g., large interfacial areas having highly reactive surfaces). In this work, the influence of various synthesis parameters (reaction temperature, stirring speed, pH value) on the size and morphology of synthesized copper oxide was investigated.

2. Experimental and Results

In a typical synthesis procedure, copper nitrate trihydrate was dissolved in distilled water while being stirred. NaOH was gradually added to the cupric chloride solution, causing blueish $Cu(OH)_2$ precipitates to immediately appear. After stirring for an additional 60 minutes, the solution was loaded into a hydrothermal reaction autoclave. Filled with distilled water to 80% of the total volume, the autoclave was held at various temperatures for 12 hours, and then cooled to room temperature. The resulting dark precipitates were centrifuged and washed with distilled water several times. Powder X-ray diffraction (XRD) patterns of all samples were measured on a X-ray diffractometer (Mac Science Corp. M03XHF, Japan) with CuK radiation at room temperature. The scan rate of 4˚/min was applied to record the pattern in the 2θ range of 20–60˚. All reflections on the pattern corresponded to the monoclinic CuO phase with lattice constants comparable to the reported data (JCPDS #45-0937). Reflection peaks from impurities were not observed in the sample. XRD analysis indicates that copper oxide was successfully created via a hydrothermal synthesis route, as shown in Fig. 1(d).

Fig. 1 shows the SEM images of copper oxide synthesized at 120˚C from solutions with different pH values. In this investigation, it was found that the pH of the solution has a significant influence on the final product morphology. It was observed that when the pH=11.0 (Fig. 1(b)), a rod-like morphology resulted (aspect ratio ~5). The as-prepared copper oxide is hydrophilic, which can be wetted and easily dispersed in water. With an increasing pH value, the morphology of the crystallites becomes more shuttle-like. Overall, the as-prepared cupper oxide crystals had a uniform morphology, which could be produced in large quantities. For the situation where pH=9.0 (Fig. 1(a)), some agglomeration of lenticular particles can be observed, and the obtained crystals are irregular in nature. The particles are elliptical in shape, not unlike those reported by Li et al [4]. It can be noted that the uniformity of morphplogy and particle size increases with increasing solution pH. Also, when the solution pH=13.0 (Fig 1(c)), thinner plates having rectangular cross-sections are observed. The particle size distribution was also investigated. The average sizes of particles produced at pH values of 9.0, 11.0, and 13.0 correspond to 1.35 μm, 0.46 μm, and 0.58 μm, respectively.

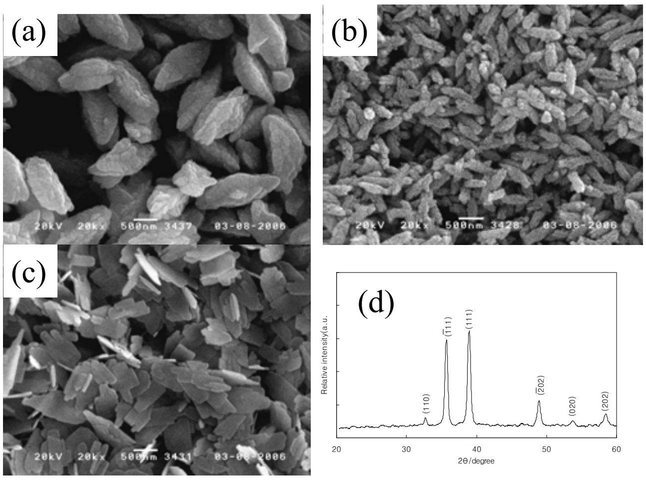

Fig. 1. SEM images and XRD pattern of copper oxide btained at 120˚C (stirring speed=500rpm, reaction time=12h) for (a) pH=9.0, (b) pH=11.0, and (c) pH=13.0. (d) is XRD pattern of the as-prepared copper oxide.

In this case, the pH value was a very important factor that should be considered in the hydrothermal synthesis of rod-like copper oxide. The influence of the morphology of $Cu(OH)_2$ on the morphology of the final product was investigated. The morphology of $Cu(OH)_2$ has a very strong correlation to the pH value. When the pH value was above pH=11.0, the morphology of $Cu(OH)_2$ was needle-like. Therefore, it would appear that morphology control of final product depends primarily on the morphology of the seed material, $Cu(OH)_2$. However, for pH=13.0, the morphology of the seed materials was needle-like, but the morphplogy of the final product was shuttle-like. This indicates that the pH value is also a factor, affecting not only the growth rate of the crystals but also the morphology of the final product.

The influence of reaction temperature on the formation of copper oxide was also investigated. If the temperature was lower than 80˚C for 12h, the formation of copper oxide crystals was incomplete, and blueish $Cu(OH)_2$ existed in the solution. At typical reaction temperatures (more than 80˚C), the hydrothermal reaction to form copper oxide is completed, as evidenced by the colorless nature of the solution after the reaction. The influence of reaction time on the formation of copper oxide crystals was also investigated. When the reaction time is less than 10h at 80˚C, the blueish $Cu(OH)_2$ was still present in the solution. If the reaction temperature increased to above 200˚C, a final product with reddish-colored impurities (Cu_2O) was observed. In this case, the oxidation state of copper was reduced from Cu^{2+} to Cu^{+}. These results are in accordance with other researchers' findings [1,2]. Therefore, the essential conditions for the synthesis of phase-pure (no impurities) copper oxide crystals using this technique is a reaction temperature of 80–170˚C, a pH of 11.0, and a 12 hour reaction time.

Fig. 2 illustrates the influence of stirring speed on the control of seed material ($Cu(OH)_2$) size at pH=11.0 and 120˚C. The stirring speed dependence of the synthesized $Cu(OH)_2$ was high, since the available nuclei concentration and growth rate affects the final product size. When the stirring speed was 200 rpm, the average particle size and particle size distributions were larger than those of the higher stirring speed (500 rpm), as shown in Fig. 2. When the stirring speed increased, the average particle size decreased. Therefore, the formation of small seed particles in a solution can greatly increase the rate at which crystals nucleate [5]. This process is understood, at least qualitatively, when the seed has same morphology as the final crystals that it spawns. However, the mechanism of seeding by a foreign substance is, at this point, not well characterized.

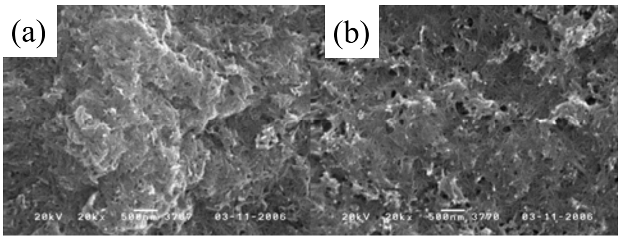

Fig. 2. SEM images of the $Cu(OH)_2$ obtained at 25˚C (pH=11) and stirring speed of (a) 200 rpm, and (b) 500 rpm.

3. Summary

Rod-like copper oxide crystals were successfully prepared using a simple and convenient hydrothermal reaction process. The final crystals had various morphologies, a uniform size distribution, and a high yield. It was found that pH value and stirring speed significantly affect overall crystal morphology as well as crystal size. Specifically, the shape of crystals is most strongly affected by the pH value. Also, the formation of smaller $Cu(OH)_2$ starting material enables the fabrication of smaller copper oxide crystals, whose morphology depends on the pH value.

4. References

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