

Synthesis and Optical Properties of CuO Nanocrystals with Controllable Shapes and Size

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Abstract: Highly dispersed copper oxide (CuO) nanoparticles had been successfully prepared by a hydrothermal technique where different adding temperatures of NaOH were taken. The as-prepared CuO nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and Raman spectroscopy. The results showed that the adding temperature of NaOH has an important influence on the shape and size of CuO nanocrystals. The influence of reaction conditions on morphology of CuO nanocrystals was discussed. Furthermore, different shapes of obtained CuO nanocrystals exhibit different Raman properties.

1 Introduction

Nano-structured transition metal oxides (MOs) are the indisputable prerequisite for the development of various novel functional and smart materials. These transition MO nanocrystals have been attracting much attention not only for fundamental scientific research, but also for various practical applications because of their unique physical and chemical properties [1]. As an important p-type semiconductor metal oxide with a narrow band gap (1.2 eV), copper oxide (CuO) has been extensively studied because of its diverse applications as material for heterogeneous catalysts, gas sensors, optical switch, magnetic storage media, field emission devices, solar cells, etc[2]. CuO nanostructures are also considered as electrode materials for the next-generation rechargeable lithium-ion batteries (LIBs) because of their high theoretical capacity, safety, and environmental friendliness. They are also promising materials for the fabrication of solar cells because of their high solar absorbance, low thermal emittance, relatively good electrical properties, and high carrier concentration.

Research on nanoparticles has gathered wide attention during the last decade because of their unusual and size dependent optical, magnetic, electronic, and chemical properties. To fully utilize these properties, the size and shape must be well controlled. Some synthesis methods are successful for fabricating shape-controlled nanocrystals of metals, semiconductors and complex metal oxides [3]. In recent years, the shape controlled synthesis of nanostructured CuO has attracted considerable attention. However, the exciting techniques have to rely on the proper selection of expensive surfactants or high crystallization temperatures. Therefore, seeking a simple strategy for low-cost, low-

temperature, controlled synthesis of oxide nanostructures at mild conditions is highly desired, and it is important as well for exploring zero- and one-dimensional oxide-based nanostructures for applications in nanodevices [4]. Here, we describe a simple procedure for the synthesis of shape-controlled CuO nanocrystals. Here we use hydrothermal synthesis of CuO nanoparticles which is generally based on a two-step process. First, cupric hydroxide [Cu(OH)₂] particles are formed by the reaction of a cupric salt precursor with a basic solution, such as sodium hydroxide (NaOH) or ammonium hydroxide. The Cu(OH)₂ particles are then thermally dehydrated in an autoclave at fixed temperatures to obtain the final CuO nanoparticles. With the hydrothermal techniques different sized CuO nanocrystals can be obtained by modulating the adding temperatures of NaOH. The method provides a convenient, low-cost, nontoxic route for the synthesis of nanostructures of oxide materials.

2 Experimental

2.1. Sample Preparation

Analytically pure Cu(NO₃)₂ and NaOH were used as the starting materials without further purification. In a typical procedure, two identical sets of 300mL of 0.02M Cu(NO₃)₂ solution were prepared by dissolving Cu(NO₃)₂·3H₂O in deionized water. Each set of solution was added into a round-bottom flask equipped with a refluxing device. The two sets of Cu(NO₃)₂ solution were kept at an appropriate temperature (60°C and 100°C, respectively) with vigorous stirring; then 0.50 g of solid NaOH (platelets) was rapidly added into each set of solution, where a large amount of black precipitate was

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simultaneously produced and maintained at the crystallization temperature for 10 min. After all reactions were completed, the resulting products were centrifuged, washed with water and ethanol for several times, and dried in air at room temperature.

2.2 Characterization

Crystal structure identification was made by X-ray diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer with Cu K α ($\lambda = 0.15405$ nm) radiation. Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM-2100 microscope operating at 200 kV, by depositing a drop of CuO dispersion onto 300 mesh Cu grids coated with carbon layer. Laser Raman Spectroscopy (LRS) studies were carried out using a Renishaw Invia Raman spectrometer from 100 to 700 cm $^{-1}$ at room temperature.

3. Results and discussion

XRD pattern (Fig. 1) of the products obtained is identical to the single-phase CuO with a monoclinic structure and the diffraction data are in good agreement with JCPDS card of CuO (JCPDS 80-1268). No peaks of impurity are observed in the XRD pattern. The broadening of the peaks indicates the small size of the products [5]. Actually, the average sizes of the CuO nanocrystals prepared at adding temperatures of 60°C and 100°C, are estimated to be 15 and 16 nm, respectively, according to the Scherrer equation. It was found that the adding temperature of NaOH has an important influence on the shape and size of CuO nanocrystals.

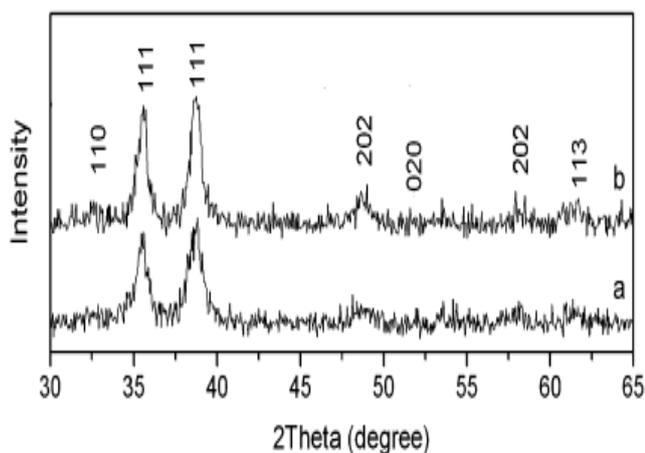
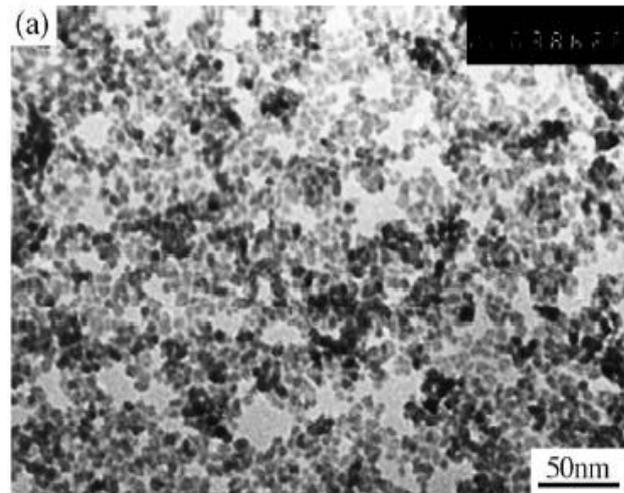
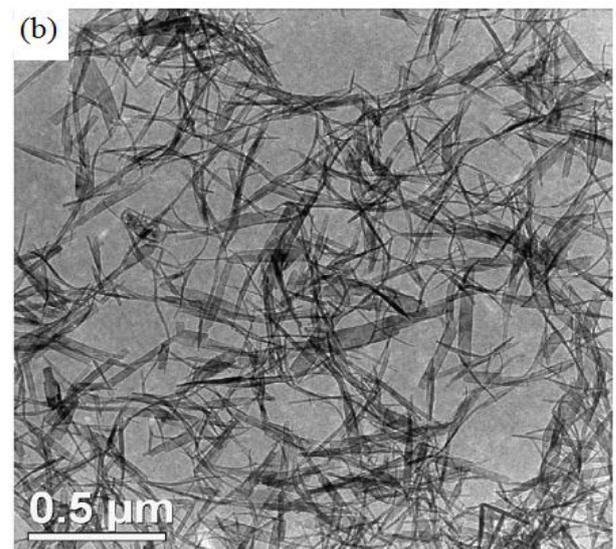


Figure 1. XRD patterns of CuO products prepared at different adding temperatures of NaOH: (a) 100 °C [4]; (b) 60 °C [4]

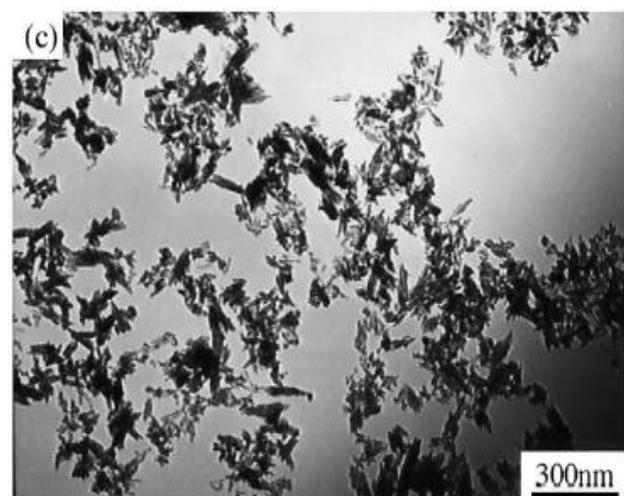
As can be seen from Fig. 2a, the nanorods with diameters of 5 nm and lengths of 25–40 nm were formed when NaOH was added at 100°C. When the adding temperature decreased to 60°C, the CuO nanobelts with diameters of 8–40 nm and lengths up to 1.0 μ m were obtained (Fig. 2b).



(a)



(b)



(c)

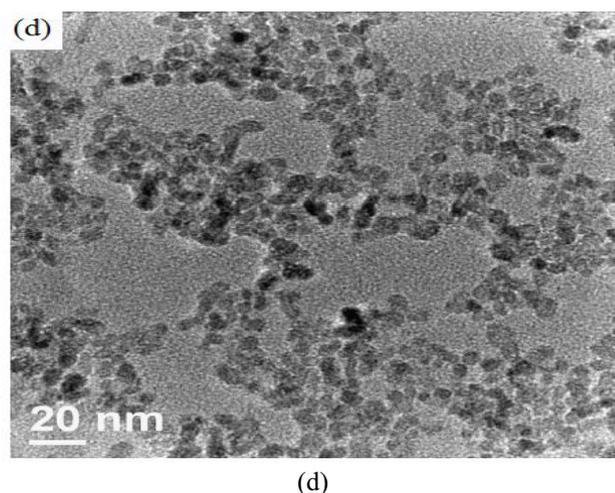


Figure 2. TEM images of the as-prepared CuO nanoparticles: **(a)** adding NaOH at 100°C [4]; **(b)** adding NaOH at 60°C [4]; **(c)** in the absence of glacial acetic acid and NaOH [6]; **(d)** in the presence of glacial acetic acid and NaOH at 100°C [4].

Typical TEM image of the as-prepared CuO nanoparticles is presented in Fig. 2, showing that the products are composed of spherical particles with narrow size distribution and high dispersion. The size of the particles observed in the TEM image is in the range of 5–7 nm, which is in good agreement with that estimated by Scherrer equation from the XRD pattern.

It is also important to point out that adding a small quantity of glacial acetic acid has an important influence on the shapes of CuO crystals. As a matter of fact, the CuO sample had been prepared by adding solid NaOH into Cu(NO₃)₂ solution at 100°C in the presence of 1mL glacial acetic acid. The TEM analysis shows that the obtained black precipitate consists of 8 nm sized spherical particles. In this method, the additive glacial acetic acid was used to prevent the hydrolysis of the copper acetate solution. If glacial acetic acid was not added, the copper acetate solution would directly hydrolyze above 80°C in the absence of NaOH and form well-dispersed needle-shaped CuO nanocrystals as observed in the TEM image (Fig. 2c). The result also indicates that different morphologies of CuO nanocrystals can be obtained easily by controlling the addition of glacial acetic acid and NaOH.

Raman spectroscopy is a very useful tool for the study of phases and structures of oxide systems. The Raman frequency can shift, and bandwidth can broaden, with the decreasing microcrystal size [7-8]. Raman spectra of CuO products prepared at different adding temperatures of NaOH are illustrated in Fig. 3. For the monoclinic CuO, this belongs to the C_{2h}⁶ space group with two molecules per unit cell. There are nine zone-center optical phonon modes with symmetries 4Au + 5Bu + Ag + 2Bg. Only three Ag + 2Bg modes are Raman active [9-10]. For the sample a (Fig. 3), it can be seen that there are three Raman peaks at 283, 330 and 619 cm⁻¹, and these peaks can be assigned to one Ag and two Bg modes, respectively. And the Raman peaks of sample b (Fig. 3) have a blue shift and shift to 290, 337 and 623 cm⁻¹, respectively. It is clear that, in this case, the reaction temperature plays an

important role in the formation of highly dispersed CuO nanoparticles.

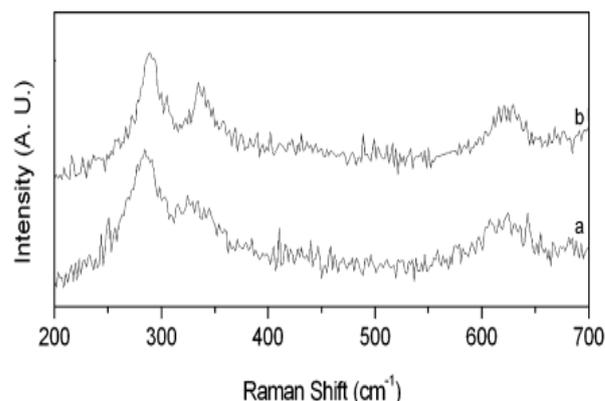


Figure 3. Raman spectra of CuO samples illustrated in Figs. 1 and 2 [4]

4. Conclusion

Well-dispersed CuO nanocrystals have been synthesized in aqueous solution via a simple hydrothermal procedure. Their shapes can be easily controlled. The shapes of CuO nanocrystals change as adding temperature of NaOH change without any additional surfactants. The adding temperatures of NaOH are critical parameters to the shape-guiding processes.

References

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