

Single-crystalline CuO Nanosheets Synthesized from a Layered Precursor

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Single-crystalline CuO nanosheets with the monoclinic structure have been successfully prepared from a layered precursor (copper(II) acetate hydroxide) in aq NaOH solution by microwave heating or hydrothermal method at 100–200 °C. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and selected area electron diffraction (SAED).

In recent years, much efforts in the field of nanomaterials have been focused on fabricating one-dimensional nanowires, nanorods, and nanotubes.¹ Two-dimensional nanosheets can be regarded as a new class of nanostructured materials because of their high anisotropy and nanometer scale thickness, possessing interesting properties.^{2–4} Nanosheets are considered as ideal systems for investigating dimensionally confined transport phenomena and regarded as the ideal base to build functional devices on them. However, only a few kinds of nanosheets have been reported up to now. For example, nanosheets of titania,^{3,5} manganese dioxide,⁶ and niobate^{7,8} were synthesized by delamination of the layered precursor. Ga₂O₃ nanosheets and nanoribbons were synthesized by evaporating GaN at high temperatures in the presence of oxygen.⁹ ZnO nanosheets were synthesized by oxidation of Zn nanosheets⁴ and by heating a mixture of ZnO and graphite at 800–950 °C in O₂ and Ar.¹⁰ Recently, we have demonstrated that single-crystalline NiO nanosheets could be synthesized by thermal decomposition of β -Ni(OH)₂ nanosheets.¹¹

CuO, a p-type semiconductor with a narrow band gap, has a wide range of applications. It has been studied extensively as a component of high-*T_c* copper oxide superconductors. High optical absorption coefficient in the visible range and reasonably good electrical properties make it suitable for fabrication of solar cells. CuO is also widely used in applications such as catalyst¹² and gas sensors.¹³ However, to the best of our knowledge, there have been no reports on the synthesis of CuO nanosheets. CuO nanosheets are difficult to synthesize because its structure is not layered. Recently, we have synthesized single-crystalline CuO nanoleaves by the microwave heating method.¹⁴ Herein, we report a new simple method for the synthesis of single-crystalline CuO nanosheets from a layered precursor.

All of the chemicals used were analytical grade. Copper acetate, ethylene glycol (EG) and NaOH were used as purchased without further purification. Typically, the precursor, copper(II) acetate hydroxide, was synthesized as follows: 0.40 g of Cu(CH₃COO)₂·H₂O and 0.16 g of NaOH were added into 20-mL of EG in a 50-mL round-bottomed flask under magnetic stirring. The mixture was heated by microwave to 140 °C and held at this temperature for 5 min. The microwave oven (2.45 GHz) used was a focused single-mode microwave synthesis system

(Discover, CEM, USA), equipped with a magnetic stirring and a water-cooled condenser. Temperature was controlled by automatically adjusting microwave power. After the mixture was cooled to room temperature, the product was separated by centrifugation and washed with absolute ethanol twice. Sample 1 was synthesized as follows: the precursor synthesized by the above method was dispersed in 20 mL of 0.1 M aq NaOH solution by ultrasonic. The solution was heated by microwave at 100 °C for 5 min. Samples 2 and 3 were prepared by the procedure similar to sample 1 except that heating times were 15 and 45 min, respectively. Sample 4 was synthesized as follows: the precursor synthesized and 20 mL of 0.1 M aq NaOH solution were sealed into a Teflon-lined stainless steel autoclave with a capacity of 40 mL and heated at 100 °C for 10 h. Samples 5–7 were prepared by the procedure similar to sample 4, but under different conditions (100 °C, 30 h for sample 5, 150 °C, 10 h for sample 6 and 200 °C, 10 h for sample 7). The products were separated by centrifugation, washed with deionized water three times and dried in a vacuum. XRD patterns were carried out on a Rigaku D/max 2550V X-ray diffractometer with Cu K α radiation and on a Huber G 670 diffractometer using graphite-monochromatized Cu K α 1 radiation. TEM images were obtained on JEOL JEM-200CX and JEOL JEM-2010 transmission electron microscopes.

The XRD pattern of the precursor, copper(II) acetate hydroxide, is shown in Figure 1a. The strong peak in the pattern corresponds to an interlayer spacing of 8.35 Å, which is typical of the corresponding layer-structured material.¹⁵ In XRD patterns of sample 1 (Figure 1b) and sample 4 (Figure 1c), all peaks can be indexed to a single phase of crystalline CuO with the monoclinic structure (JCPDS No.80-1917). These results show that crystalline CuO can be prepared from the precursor, copper(II) acetate hydroxide, by the microwave heating or hydrothermal method at 100 °C. However, shorter time was needed for preparation of CuO using microwave heating compared with

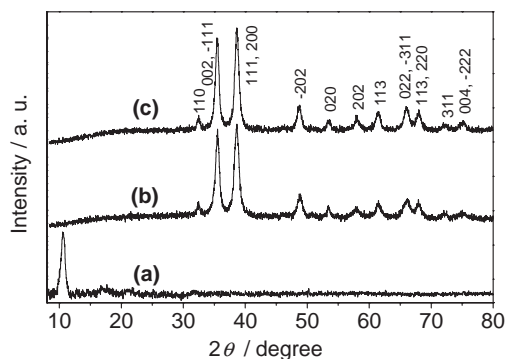


Figure 1. XRD patterns of three samples. (a) precursor; (b) sample 1; (c) sample 4.

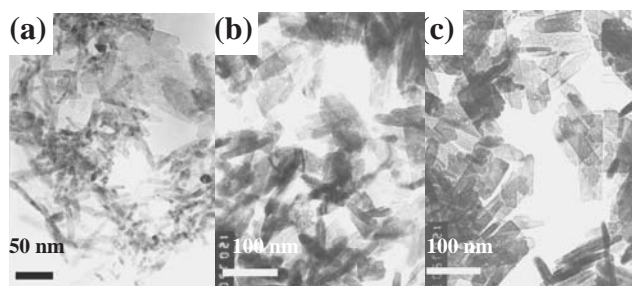


Figure 2. TEM micrographs of three samples. (a) sample 1; (b) sample 2 and (c) sample 3.

hydrothermal heating. The XRD showed that the crystallinity of CuO prepared by microwave heating at 100 °C for 5 min was better than that prepared by hydrothermal heating at 100 °C for 1 h. The yield of the products was $\approx 91\%$.

The morphology and microstructure of the products were investigated by TEM and SAED. Figure 2 shows TEM micrographs of samples 1–3 prepared by microwave heating. Figure 2a shows TEM micrograph of sample 1 prepared by microwave heating for 5 min, from which one can see nanorods with diameters in the range of 10–20 nm and lengths up to ≈ 120 nm. In addition to nanorods, nanosheets were also observed as the minor morphology. From Figures 2b (sample 2) and 2c (sample 3), one can see that the proportion of nanosheets increased by increasing microwave heating time. Sample 3 prepared by microwave heating for 45 min consisted mainly of quasi-rectangular nanosheets with lateral sizes up to 150 nm.

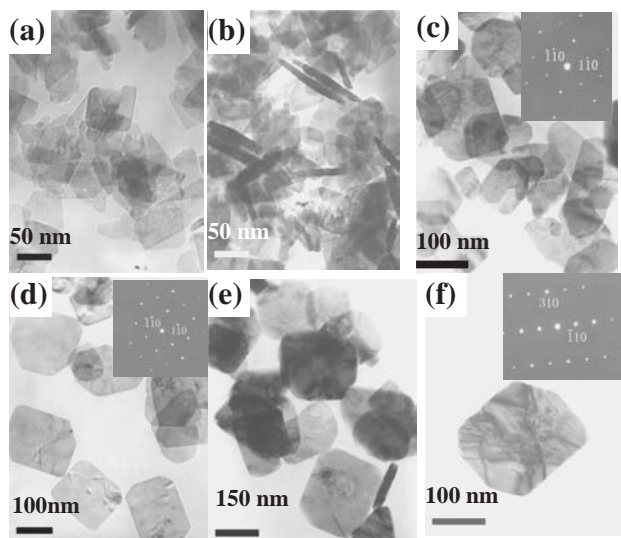


Figure 3. TEM micrographs and SAED patterns of four samples. (a) and (b) sample 4; (c) sample 5; (d) sample 6; (e) and (f) sample 7. The insets of (c), (d) and (f) show the SAED patterns of individual nanosheets obtained by focusing the incident electron beam along the [001] zone axis.

Hydrothermal heating instead of microwave heating was also used for the preparation of CuO nanosheets. Figure 3 shows TEM images of samples 4–7 prepared by the hydrothermal method. Figures 3a and 3b show TEM micrographs of sample 4 prepared by hydrothermal treating at 100 °C for 10 h. Most of CuO nanostructures are irregularly shaped nanosheets with

lateral dimensions in the range of 25–80 nm. A small number of nanorods were also observed with diameters of 15–20 nm and lengths up to ≈ 100 nm (Figure 3b). Sample 5 prepared by hydrothermal treating at 100 °C for 30 h consisted of nanosheets with well-developed crystallographic facets and with lateral sizes in the range of 70–250 nm (Figure 3c). Many CuO nanosheets have angles between adjacent facets of 90°, 126°, and 144°, in good agreement with the theoretical values (90° for the angle between [100] and [010], 126.15° for the angle between [010] and $[\bar{1}10]$, 143.85° for the angle between [100] and $[\bar{1}\bar{1}0]$). We suggest that the surface of the nanosheets is the {001} planes of the monoclinic CuO. Figure 3d shows a TEM image of sample 6 prepared by hydrothermal method at 150 °C for 10 h and Figures 3e and 3f for sample 7 at 200 °C for 10 h. One can see that CuO nanosheets with more regularly crystallographic morphologies and larger lateral sizes were produced by increasing the temperature. The SAED patterns of single nanosheets shown in the insets of Figures 3c, 3d, and 3f indicate that CuO nanosheets are single crystalline in structure. The SAED patterns can be indexed with the monoclinic CuO structure, consistent with the result obtained from XRD.

In summary, powders of single-crystalline CuO nanosheets with the monoclinic structure have been successfully synthesized from a layered precursor, copper(II) acetate hydroxide, in aq NaOH solution by microwave heating or hydrothermal method at 100–200 °C. This method is simple and low-cost for large-scale production of powders of single-crystalline CuO nanosheets. We expect that this layered precursor conversion method can be extended to synthesize nanosheets of other kinds of metal oxides.

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