

CuO Nanotubes Synthesized by the Thermal Oxidation of Cu Nanowires

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Copper oxide (CuO) is a narrow band-gap semiconducting oxide that has been widely used as a cathode in dye-sensitized solar cells, gas sensors and heterogeneous catalysts.¹⁻³ Much effort has been devoted to synthesizing unique CuO nanostructures, such as, rods, wires, ribbons, cubes, spheres and dandelions.⁴⁻¹⁰ Unlike nanorods and nanowires, only a few groups have synthesized CuO nanotubes due to fabrication difficulties within hollow nanorods and nanowires. CuO nanotubes were synthesized by pyrolyzing copper acetylacetonate within the pores of the anodic alumina membranes.¹¹ CuO nanotubes of average length 100 nm were also synthesized by a hydrothermal process involving microemulsified $\text{Cu}(\text{OH})_4^{2-}$.¹² The simplest method of making CuO is from the direct thermal oxidation of copper metal,¹³ and many research groups have prepared CuO nanowires and nanorods by oxidizing copper foils.¹⁴⁻¹⁶ However, due to self aggregation, it is difficult to obtain long copper nanowire or nanorod precursors for the preparation of CuO nanotubes by direct thermal oxidation. Here, we describe the preparation of CuO nanotubes from long copper nanowires by simple thermal oxidation. The morphologies of the CuO nanotubes produced were determined by scanning electron microscopy and transmission electron microscopy.

Experimental Section

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99%, Aldrich), N,N,N',N'-tetramethylethylenediamine (TMEDA, 98%, TCI), cyclohexane (99%, Aldrich), glucose (99.5%, Aldrich) and cetyltrimethylammonium bromide (95%, CTAB, TCI) were used as received. To prepare the copper nanowires, we used a CTAB/TMEDA/water/cyclohexane system. Briefly, 2.4 mL of TMEDA and 8 mmol of glucose were added to 20 mL of a 0.2 M CuCl_2 aqueous solution with stirring. After allowing this mixture to stir for 5 min, 1.6 g of CTAB and 40 mL of cyclohexane were added. This reaction solution was then transferred to a 100 mL Teflon-lined autoclave and heated at 120 °C for 24 h. The system was then allowed to cool to room temperature. The copper nanowires produced were obtained by filtering, washing several times with ethanol, and drying at 60 °C for 12 h. These nanowires were used to prepare CuO nanotubes by simple thermal oxidation. Briefly, copper nanowires were placed in an alumina crucible, which was then heated in a box-type furnace at 400 °C for 5 h. During the course of this study, we used other calcination temperatures to investigate nanotube formation.

The structures of the copper nanowires and CuO nanotubes produced were analyzed by powder X-ray diffraction (XRD, PANalytical, X'pert PRO MPD) using $\text{Cu K}\alpha$ radiation, and their morphologies were determined by scanning electron microscopy (SEM, Hitachi S-4300) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3010).

Results and Discussion

Figure 1 shows SEM images of copper nanowires prepared using a CuCl_2 aqueous solution with glucose in the CTAB/TMEDA/water/cyclohexane system using a hydrothermal process at 120 °C for 24 h. Glucose and CTAB were used as a reducing agent and soft template, respectively. A large quantity of uniform nanowires of length up to 50 μm and diameter of *ca.* 200-800 nm were formed. Figure 2(A) shows the XRD pattern of a copper nanowire. All peaks were assignable to cubic copper metal and concurred with literature data (JCPDS 04-0836, $a = 3.615 \text{ \AA}$). Since no other peaks were detected, we presume that the ultra long copper nanowires produced were effectively free from impurities. The synthetic method used in this study and the mechanisms of copper nanowire formation using various amines and organic solvents have been previously described in detail.¹⁷

In order to optimize calcination temperature for nanotube formation, we studied the surface morphologies of CuO nanotubes prepared at different temperatures. SEM images of CuO nanotubes prepared by oxidizing copper nanowires at temperatures from 300 °C to 600 °C in air for 5 h are shown in Figure 3. Nanotubes with open ends were obtained from 300 °C. On increasing calcination temperature beyond

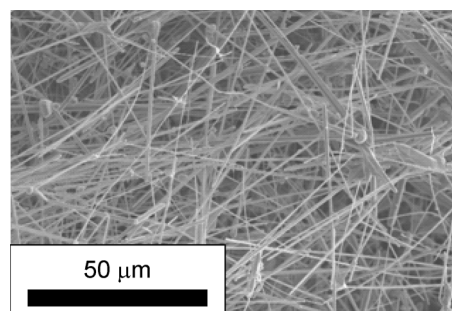


Figure 1. SEM image of copper nanowires synthesized by a hydrothermal process in the CTAB/TMEDA/water/cyclohexane system.

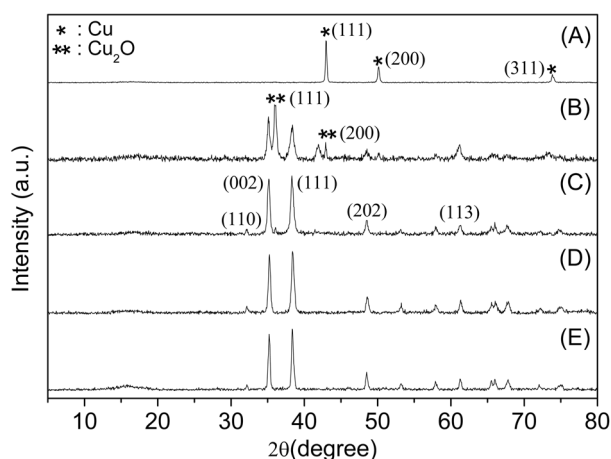


Figure 2. X-ray diffraction patterns of (A) copper nanowires synthesized by the hydrothermal process and CuO products synthesized by direct thermal oxidation of copper nanowires at different temperatures; (B) 300 °C, (C) 400 °C, (D) 500 °C, and (E) 600 °C. The single and double asterisks denote Cu and Cu₂O, respectively.

500 °C, large grains formed on the surfaces of nanotubes, and nanotube formation was totally disrupted by the formation of large surface grains at 600 °C. Figure 2(B) shows the XRD pattern of CuO nanotubes obtained by oxidizing copper nanowires at 300 °C. Most of the peaks observed corresponded to those of pure monoclinic CuO (JCPDS 45-0937, $a = 4.6837 \text{ \AA}$, $b = 3.4226 \text{ \AA}$, $c = 5.1288 \text{ \AA}$, $\beta = 99.54^\circ$).¹⁸ In addition, peaks indexed as (111) and (200) diffractions of cubic Cu₂O were observed (JCPDS 05-0667, $a = 4.2696 \text{ \AA}$). However, all observed peaks were matched with pure CuO patterns at above 400 °C, indicating that pure CuO tube-like products can be obtained by calcination copper nanowires at 400 °C. Based on the XRD data obtained, we suggest that nanowire surfaces are initially oxidized to Cu₂O and that the tube structure is formed by further oxidation to CuO.

It appears that nanotube formation is associated with the consumption of copper atoms inside surface-oxidized nano-

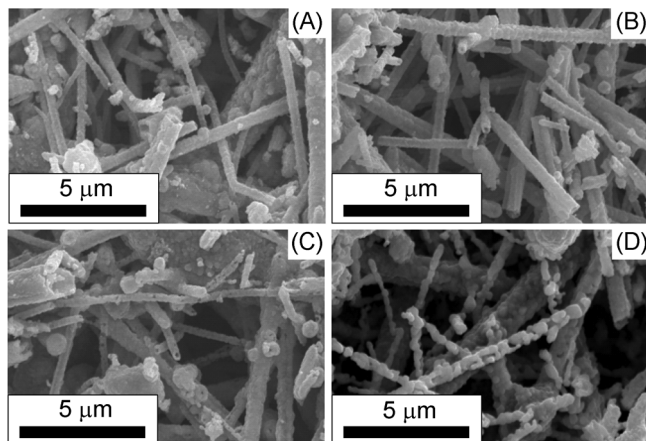


Figure 3. SEM images of CuO products synthesized *via* the direct oxidation of copper nanowires at different temperatures; (A) 300 °C, (B) 400 °C, (C) 500 °C, and (D) 600 °C.

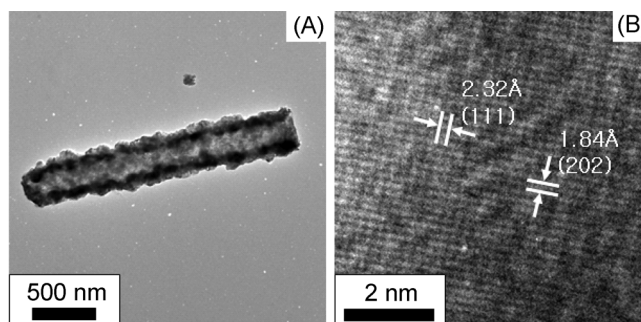


Figure 4. (A) TEM and (B) HRTEM images of CuO nanotubes obtained by the direct oxidation of copper nanowires at 400 °C.

wires. Figure 4(A) is a TEM image of a CuO nanotube. The dark and light regions provide convincing evidence of the hollow structure. The diameter and wall thickness of the CuO nanotube shown in Figure 4(A) are 370 nm and 80 nm, respectively. The length of the nanotube shown in Figure 4(A) is about 2 μm . Short nanotubes are shown to reveal the tubular structure. The average length of the CuO nanotubes made was *ca.* 10 μm , as shown in Figure 3(B), which is appreciably shorter than that of copper nanowire precursor, and was probably caused disruption during thermal oxidation. The diameter of the CuO nanotubes was *ca.* 300–800 nm, which is a little larger than that of copper nanowire precursor, as shown in Figure 3(B). This indicates that the CuO was formed at the surface of copper nanowires. Figure 4(B) shows a high-resolution TEM (HRTEM) image of the outer surface of a CuO nanotube. The fringe patterns shown indicate spacings of 2.32 \AA and 1.84 \AA , which correspond to the (111) and (202) planes of CuO, respectively.

The transformation process from Cu to CuO was investigated by SEM, TEM, and XRD. Our observations suggest that the CuO nanotubes were formed by solid-gas reactions involving diffusion of reactants. During the first step, it appears that oxygen in air reacts with the outer surfaces of copper nanowires to produce a Cu₂O layer, which are transformed to CuO by further oxidation. We suggest that this CuO layer acts as an interface, which separates the inner unreacted copper and gaseous oxygen. Thus, the reaction appears to proceed via the diffusion of both copper and oxygen. Accordingly, oxygens diffuse from the outside to the inside and copper vapors move in the opposite direction, in accord with Fick's first law. This might be a sort of the Kirkendall effect.¹⁹ We presume that the copper vapors effectively diffuses toward the surface to react with oxygen and create the tubular structure of CuO.

Summarizing, ultralong copper nanowires of length up to 50 μm were prepared by reducing a copper-TMEDA complex in an aqueous-cyclohexane bilayer system using CTAB as a soft template, and used as a sacrificial template to produce CuO nanotubes of length *ca.* 10 μm by simple oxidation in air at 400 °C. We suggest that the tubular structure is produced by copper diffusing from the interior to the exterior of nanowires prior to its oxidation on or near the surface.

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