Synthesis of CuO Wires from Layered Organic-Inorganic Hybrids

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Copper oxide (CuO) is a narrow band-gap semiconducting oxide that has been widely studied in electrochemical cells, in photothermal and photoconductive materials, and as a heterogeneous catalyst.[1-3] Various techniques have been used to fabricate CuO nanostructures.[3-6] One-dimensional (1D) CuO can be obtained through thermal treatment by using the precursors $Cu(OH)_2$ or $Cu_2(OH)_2CO_3$ as a sacrificial template.[7-9] Layered organic-inorganic hybrids are characterized by strong intralayer covalent or ionic bonding in an inorganic frame, and weak interlayer interactions such as van der Waals forces between organic molecules.[10-14] Most layered organic-inorganic hybrid materials fabricated to date were obtained by intercalation of organic molecules into the inorganic layer. In this work, we report the preparation of CuO from the layered organic-inorganic hybrid, $Cu_2(OH)_3(C_{12}H_{25}SO_4)$. CuO wires are formed by a self-aggregation of nanoparticles. The morphologies of the aggregated CuO products are analyzed using scanning electron microscopy and transmission electron microscopy.

Experimental Section

The layered organic-inorganic compound $Cu_2(OH)_3$-$(C_{12}H_{25}SO_4)$ was prepared by slow titration of a mixed solution containing 100 mL of $Cu(NO_3)_2 \cdot 2.5H_2O$ (8.6 mmol), 100 mL of $C_{12}H_{25}SO_4Na$ (4.3 mmol), and 100 mL of NaOH (13.0 mmol). The resulting precipitate was aged at room temperature for 7 days. The products were filtered, washed with water to remove unreacted sodium dodecylsulfate and impurities, and dried under vacuum at room temperature. CHN elementary analysis was used to confirm the product. Anal. calcd. (found) for $C_{12}H_{28}O_7SCu_2$: C, 32.5 (32.4), H, 6.4 (6.7), N; 0.0 (0.0). The CuO was synthesized by thermal decomposition of $Cu_2(OH)_3(C_{12}H_{25}SO_4)$ at 850 °C for 1 h.

The structures of $Cu_2(OH)_3(C_{12}H_{25}SO_4)$ and CuO were analyzed by powder X-ray diffraction (XRD, Phillips PW 1710) using Cu K_α radiation. The morphology of the CuO was characterized by scanning electron microscopy (SEM, Phillips XL30 ESEM-FEG) and transmission electron microscopy (TEM, Jeol 2010). The thermal behavior of the precursor was studied by thermogravimetric analysis (TGA, Seiko Exstar 6000).

Results and Discussion

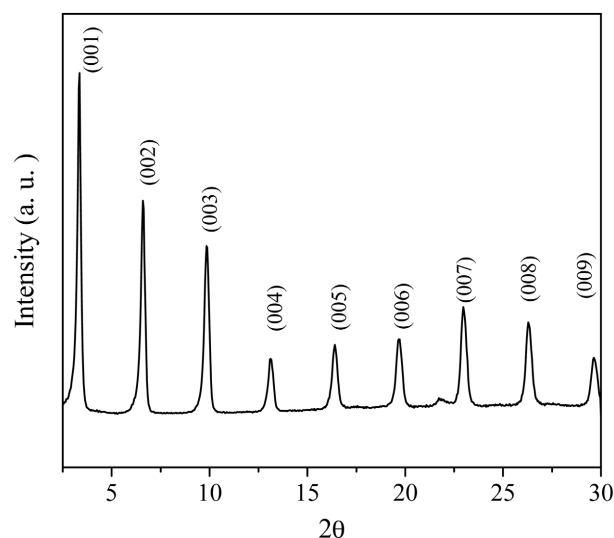The copper hydroxide salts, $Cu_2(OH)_3X$ (X = exchange-

Figure 1. X-ray diffraction pattern and Miller indices of $Cu_2(OH)_3(C_{12}H_{25}SO_4)$.

able anion, NO_3^-, $RCOO^-$, etc.), show a botallackite-type structure, in which two distinct copper atoms lie in 4 + 2 (oxygen + X) and 4 + 1 + 1 (oxygen + oxygen + X) environments.[15,16] The anion is located in the interlayer, while the molecular component coordinates the copper ion. The copper hydroxide salts form plate-like structures. The interlayer distance depends on the intercalated organic moiety. Figure 1 shows the X-ray diffraction pattern and Miller indices of $Cu_2(OH)_3(C_{12}H_{25}SO_4)$. The series of (*00l*) peaks at regular intervals indicates a typical layered structure. The basal spacing is calculated to be 26.2 Å, which is equal to that reported by Rabu *et al*.[17,18] The interdigitated monolayer structure of the dodecylsulfate is oriented normal to the $[Cu_2(OH)_3]^+$ layer.

Figure 2 shows a typical TGA curve for the $Cu_2(OH)_3$-$(C_{12}H_{25}SO_4)$ precursor in an atmospheric flow. The curve shows four pronounced weight loss steps. The first weight loss at 45 °C is due to the dehydration of water adsorbed within the precursor, where the actual empirical formula for the precursor is $Cu_2(OH)_3(C_{12}H_{25}SO_4) \cdot 0.38H_2O$. Between 180 °C and 250 °C, there is a major weight loss due to the decomposition of intercalated dodecylsulfate where the suggested product is the stable $CuO \cdot CuSO_4$.[19] The calculated and measured weight losses are 46.9% and 48.6%, respectively. The third weight loss is observed in the temperature range of 250-410 °C. In this temperature range,
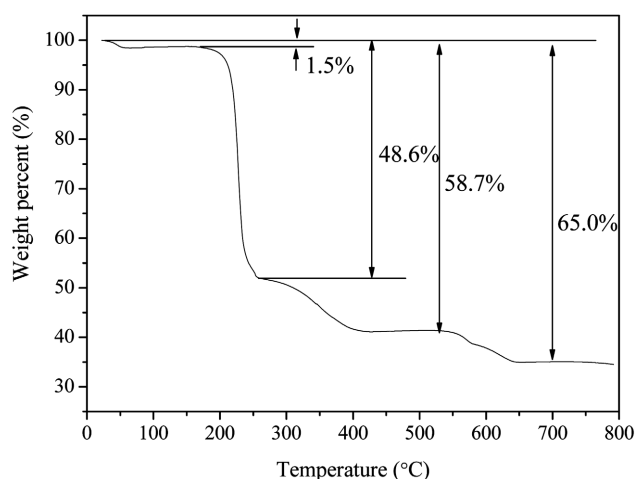
Figure 2. TGA curve of $Cu_2(OH)_3(C_{12}H_{25}SO_4)$.

Figure 4. TEM image of CuO product obtained from the $Cu_2(OH)_3(C_{12}H_{25}SO_4)$ precursor by thermal treatment at 850 °C.

$CuO \cdot CuSO_4$ is partially decomposed to form the more stable $1.5CuO \cdot 0.5CuSO_4$ with calculated and measured weight losses of 59.3% and 58.7%, respectively.[19] Above 650 °C, the $1.5CuO \cdot 0.5CuSO_4$ decomposes to form $2CuO$ with calculated and measured weight losses of 64.6% and 65.0%, respectively. The possible chemical reactions for the thermal decomposition of $Cu_2(OH)_3(C_{12}H_{25}SO_4) \cdot 0.38H_2O$ are presented below:

$$Cu_2(OH)_3(C_{12}H_{25}SO_4)0.38H_2O$$
$$\rightarrow \; Cu_2(OH)_3(C_{12}H_{25}SO_4) + 0.38H_2O \quad (1)$$

$$Cu_2(OH)_3(C_{12}H_{25}SO_4) \; \rightarrow \; CuO \cdot CuSO_4 + C_{12}H_{25}OH$$
$$+ \; H_2O \; (\text{and other forms}) \quad (2)$$

$$CuO \cdot CuSO_4 \; \rightarrow \; 1.5CuO \cdot 0.5CuSO_4 + 0.5SO_3 \quad (3)$$

$$1.5CuO \cdot 0.5CuSO_4 \; \rightarrow \; 2CuO + 0.5SO_3 \quad (4)$$
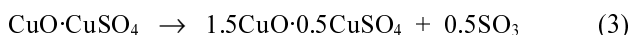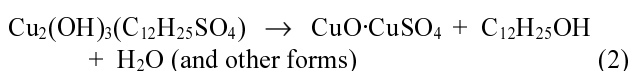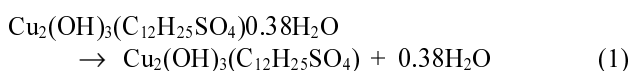
Figure 3 shows the X-ray diffraction pattern and Miller indices of CuO obtained by the thermal decomposition of $Cu_2(OH)_3(C_{12}H_{25}SO_4) \cdot 0.38H_2O$ at 850 °C for 1 h. The diffraction peaks correspond to pure CuO with a monoclinic
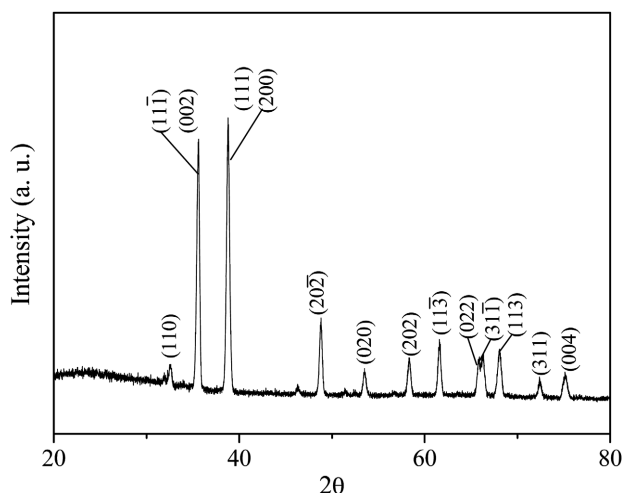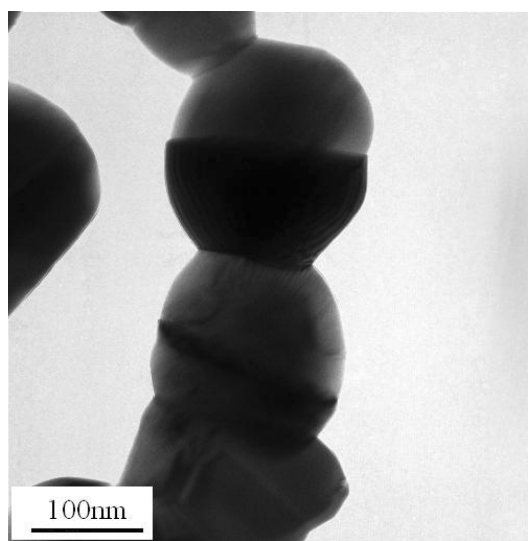
structure (a = 4.6837 Å, b = 3.4226 Å, c = 5.1288, β = 99.54°, JCPDS 45-0937).[20] The XRD peaks exhibit no broadening since the particles are much larger than the nanometer range.

Figure 4 shows the TEM images of the CuO product obtained by thermal decomposition of the $Cu_2(OH)_3$-$(C_{12}H_{25}SO_4)$ precursor at 850 °C. The image consists of a large number of particles with a fairly uniform diameter of 150 nm. Figure 5(A) shows the SEM morphology of the wire-like structure of the resulting CuO product. SEM examination shows that the CuO wires are ~1 μm thick with lengths up to 20 μm. Note that there are no flat or spherical structures. As can be seen from Figure 5(B), the CuO wire consists of particles with sizes on the order of a few hundred nanometers. The SEM image reveals that the micron-sized CuO wire is in fact an assembly of dozens of hundred nanometer-sized particles. Therefore, the CuO nanoparticles aggregate and assemble to form micron-sized CuO wires. If the aggregation and assembly of CuO particles were random, a spherical CuO product would result.

The $Cu_2(OH)_3(C_{12}H_{25}SO_4)$ precursor has a typical layered structure with a basal spacing of 26.2 Å. The $CuO \cdot CuSO_4$ product is formed by thermal decomposition of the organic dodecyl sulfate in the $Cu_2(OH)_3(C_{12}H_{25}SO_4)$ precursor at 200 °C. Since the interlayer distance is relative long, the layered precursor structure slowly collapses to form $CuO \cdot CuSO_4$ at this temperature, with the $CuO \cdot CuSO_4$ particles stacked layer by layer. At higher temperature, the $CuO \cdot CuSO_4$ compounds finally decompose to form CuO particles. These CuO particles aggregate in a specific way to form micron-sized CuO wire. The formation mechanism of the micron-sized CuO wire is not clear. However, the formation of aggregated CuO wires depends on the morphology of the precursor. The decomposition of the layered $Cu_2(OH)_3(C_{12}H_{25}SO_4)$ leads the CuO particles to integrate and to form wire-like CuO. The micron-sized CuO wires are

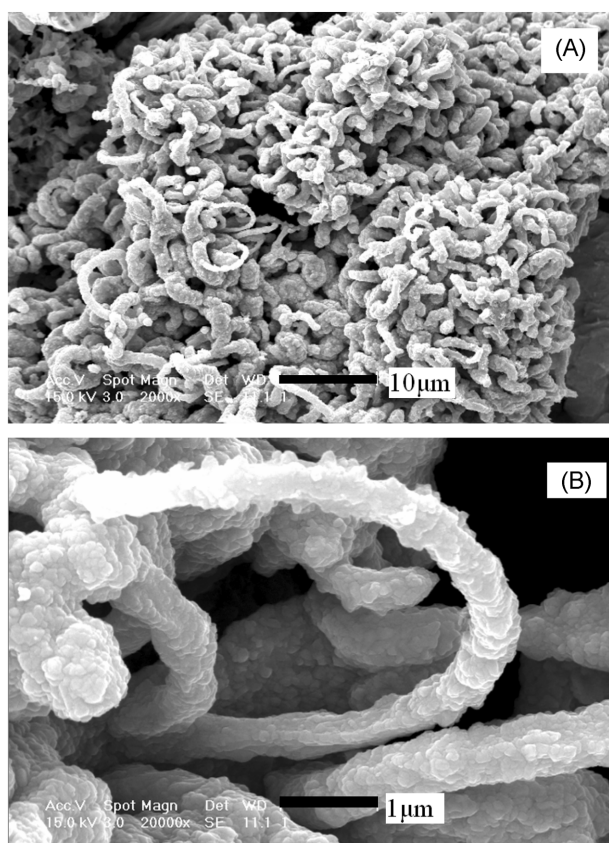**Figure 3**. X-ray diffraction pattern and Miller indices of CuO.

Figure 5. SEM images of CuO wire obtained from the $Cu_2(OH)_3(C_{12}H_{25}SO_4)$ precursor by thermal treatment at 850 °C; (A) × 2000 and (B) × 20000.

synthesized from two-dimensional (2D) $Cu_2(OH)_3(C_{12}H_{25}SO_4)$ by simple thermal decomposition in the absence of a suitable template.

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