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. Various techniques have been used to fabricate CuO nanostructures. One-dimensional (1D) CuO can be obtained through thermal treatment by using the precursors Cu(OH)$_2$ or Cu$_2$(OH)$_3$CO$_3$ as a sacrificial template. 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. 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$_3$)$_2$·3H$_2$O (8.6 mmol), 100 mL of C$_{12}$H$_{25}$SO$_4$Na (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 elemental analysis was used to confirm the product. Anal. calcd. (found) for C$_{12}$H$_{25}$O$_7$SCu$_2$: 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, Philips PW 1710) using Cu Kα radiation. The morphology of the CuO was characterized by scanning electron microscopy (SEM, Philips 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)$_3$X (X = exchangeable anion, NO$_3^-$, RCOO$^-$, etc.), show a botulackie-type structure, in which two distinct copper atoms lie in 4 + 2 (oxygen + X) and 4 + 1 + 1 (oxygen + oxygen + X) environments. 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. 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$_4$)·0.38H$_2$O. 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·CuSO$_4$. 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,
CuOCuSO₄ is partially decomposed to form the more stable 1.5CuO·0.5CuSO₄ with calculated and measured weight losses of 59.3% and 58.7%, respectively. Above 650 °C, the 1.5CuO·0.5CuSO₄ 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 Cu₄(OH)₃(C₁₂H₂₅SO₄)·0.38H₂O are presented below:

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\begin{align*}
\text{Cu}_4(\text{OH})_3(\text{C}_{12}\text{H}_{25}\text{SO}_4)·0.38\text{H}_2\text{O} & \to \text{Cu}_4(\text{OH})_3(\text{C}_{12}\text{H}_{25}\text{SO}_4) + 0.38\text{H}_2\text{O} \quad (1) \\
\text{Cu}_4(\text{OH})_3(\text{C}_{12}\text{H}_{25}\text{SO}_4) & \to \text{CuO}_2\text{CuSO}_4 + \text{C}_{12}\text{H}_{25}\text{OH} + \text{H}_2\text{O} \quad \text{(and other forms)} \quad (2) \\
\text{CuO}_2\text{CuSO}_4 & \to 1.5\text{CuO}_20.5\text{CuSO}_4 + 0.5\text{SO}_3 \quad (3) \\
1.5\text{CuO}_20.5\text{CuSO}_4 & \to 2\text{CuO} + 0.5\text{SO}_3 \quad (4)
\end{align*}
\]

Figure 3 shows the X-ray diffraction pattern and Miller indices of CuO obtained by the thermal decomposition of Cu₄(OH)₃(C₁₂H₂₅SO₄)·0.38H₂O at 850 °C for 1 h. The diffraction peaks correspond to pure CuO with a monoclinic structure (\(a = 4.6837 \, \text{Å}, \, b = 3.4226 \, \text{Å}, \, c = 5.1288, \, \beta = 99.54^\circ\), JCPDS 45-0937). 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 Cu₄(OH)₃-(C₁₂H₂₅SO₄) 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. Figure 5(B) shows that the CuO wire consists of particles with sizes on the order of a few hundred nanometers. 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.
synthesized from two-dimensional (2D) $\text{Cu}_2\text{OH}_2\text{C}_12\text{H}_{25}\text{SO}_4$ by simple thermal decomposition in the absence of a suitable template.

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References


Figure 5. SEM images of CuO wire obtained from the Cu$_2$(OH)$_2$C$_{12}$H$_{25}$SO$_4$ precursor by thermal treatment at 850 °C; (A) $\times$2000 and (B) $\times$20000.