

Mesoscale organization of CuO nanoslices: Formation of sphere

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Abstract. The nanocrystalline CuO powders were prepared by precipitation method using $\text{Cu}(\text{NO}_3)_2$ as copper raw material, water and ethanol as dispersants, and NaOH and ammonia solution as precipitates. The structure, particle size and morphology of resulting CuO powders were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The mechanism of CuO formation was discussed.

Keywords. CuO; chemical synthesis; electron microscopy.

1. Introduction

CuO is a *p*-type semiconductor with a narrow band gap ($E_g = 1.2$ eV) (Musa *et al* 1998). CuO has been used as heterogeneous catalysts in many important chemical processes such as degradation of nitrous oxide, selective catalytic reduction of nitric oxide with ammonia, and oxidation of carbon monoxide, hydrocarbon and phenol in supercritical water (Reitz and Solomon 1998; Wang H *et al* 2002; Wang W *et al* 2002). In recent studies, it was found that CuO could increase temperature of the superconductors (Wu *et al* 1987; Prabhakaran *et al* 1999; Zheng *et al* 2000; Borgohain and Mahamuni 2002). CuO can also be used as gas sensors (Poizot *et al* 2000; Zhang *et al* 2006), optical switch (MacDonald 2001), magnetic storage media (Kumar *et al* 2000), lithium batteries (Lanza *et al* 1990; Gao *et al* 2004) and solar cells (Rakhshni 1986; Maruyama 1998) owing to its photoconductive and photochemical properties.

Nanoscaled materials are of great interest due to their unique optical, electrical and magnetic properties and their potential applications in nanodevices (Iijima 1991; Favier *et al* 2001). As we know, it is extremely important to be able to control the size and morphology of the nanomaterials (Cao *et al* 2001).

In recent years, nanostructured CuO materials and assemblies have attracted considerable attention due to their fundamental and practical importance. Hu and co-workers have synthesized CuO nanotubes and nanorods by hydrothermal treatment of $[\text{Cu}(\text{OH})_4]^{2-}$ in the presence of CTAB (Cao *et al* 2003). Xia and co-workers reported the synthesis of CuO nanowires by heating copper substrates

in air within the temperature range of 400–700°C (Jiang *et al* 2002). CuO nanorods, nanoribbons and dandelion-like hollow microspheres have been fabricated in water-ethanol mixed solvent by Huachun Zeng's group (Chang and Zeng 2004; Liu and Zeng 2004). Chen and co-workers have prepared prickly CuO microspheres by a solvothermal route (Xu *et al* 2005). Li and co-workers have used mono-dispersed Cu_2O nanospheres as precursors to synthesize CuO nanospheres by gas-phase oxidation. Recently, we have successfully fabricated CuO nanotube arrays and nanoflower films on copper foil, respectively (Zhang *et al* 2006). However, it is still a challenge for us to prepare a variety of CuO nanostructures and their assemblies in the same reaction system only by manipulating reaction conditions.

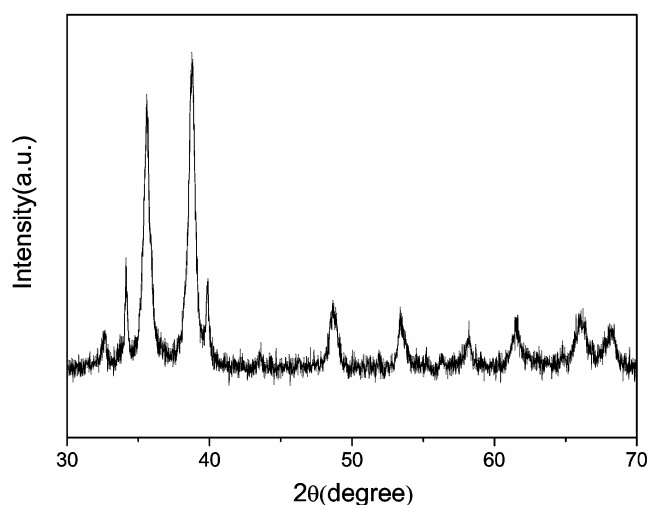


Figure 1. A representative XRD pattern recorded for CuO microspheres synthesized in this work.

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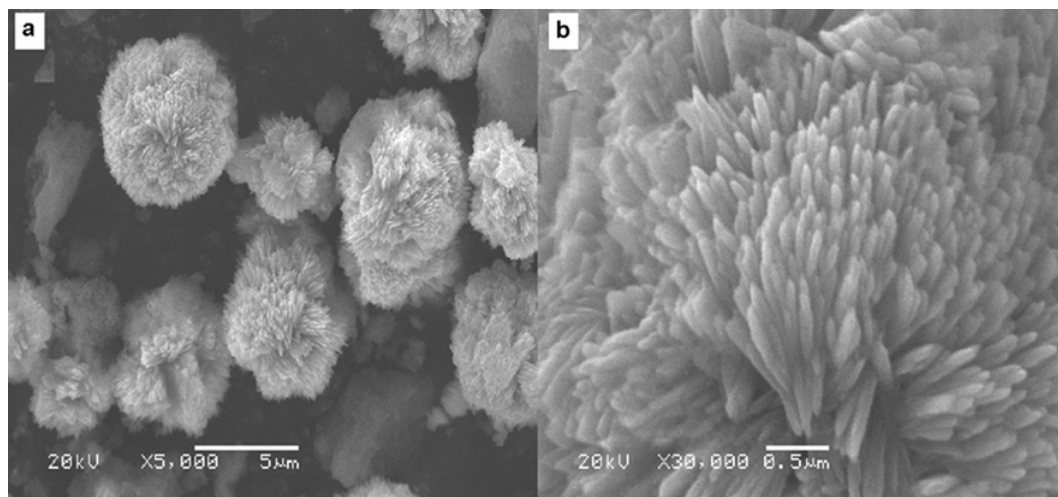


Figure 2. SEM images of CuO microspheres: **a.** overall product morphology and **b.** a detailed view on an individual sphere.

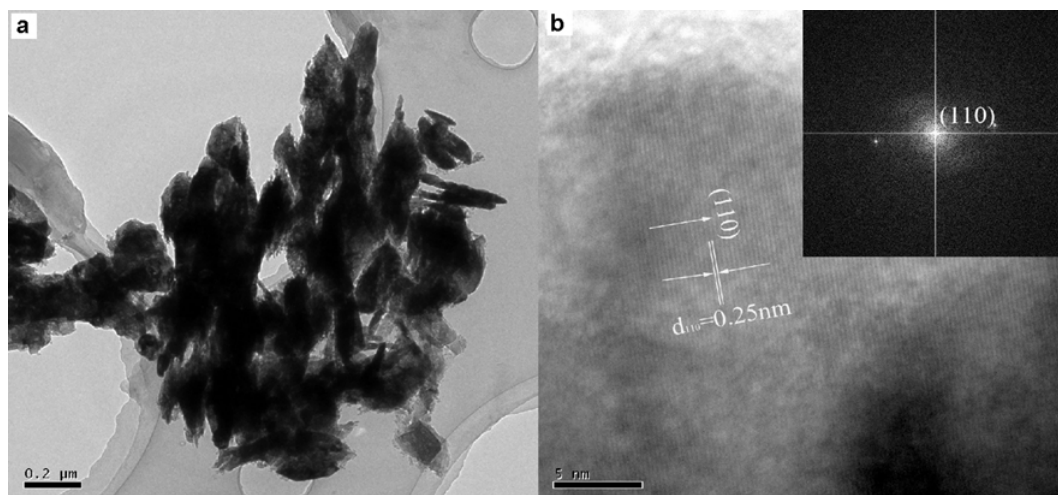


Figure 3. **a.** Low magnification TEM image of the grown CuO nanoslices and **b.** HRTEM image showing the difference between two lattice fringes, which is about 0.25 nm. Corresponding FFT pattern (inset) is consistent with the HRTEM observation.

In this work, we report a simple solution route to prepare CuO nanoslice and its spherical hierarchical assemblies. A possible illustration of the process on the morphology of CuO nanostructure is proposed. Our research results further enrich the hierarchical CuO architecture family.

2. Experimental

All the reagents were of analytical grade and were used without further purification. The starting solution of copper (1 M) was prepared by mixing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in pure ethanol solvent. Typically, 50 mL of the above solution was added with 50 mL of ammonia solution (25% ~

28%), followed by an addition of 10 mL of aqueous NaOH (1 M). The solution mixture was transferred to a Teflon-lined stainless steel autoclave which was then heated at 180°C for 5 h in an electric oven. After reaction, the autoclave was cooled at 25°C. The resultant precipitates were washed with distilled water and ethanol. Finally, the products were dried in vacuum at 60°C for 12 h. The crystallographic information was established with powder X-ray diffraction (XRD, Rigaku, $\text{Cu-K}\alpha$ radiation). The dimension, morphology, crystal lattice and composition of the obtained CuO samples were characterized with scanning electron microscopy (SEM, JSM-6480), transmission electron microscopy (TEM, PHILIPS CM 200 FEG, 160 kV).

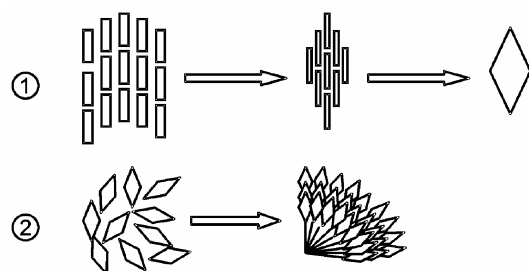


Figure 4. Illustration of formation mechanism of the sphere.

3. Results and discussion

The structure and chemical composition of CuO sample synthesized in this work was confirmed by XRD method. As reported in figure 1, typical XRD pattern for the sample is displayed. The major peaks located at 2θ values of 30° – 70° correspond to the characteristic diffractions of monoclinic phase CuO (JCPDS 48-1548), indicating that all the products were phase-pure.

Figure 2 shows general morphologies of the as-prepared CuO sample. Interestingly, the CuO crystallites self-organized into spherical assemblies with a puffy appearance. Under the reported conditions, the CuO products are all in this morphology, with diameters ranging from 5–8 μm .

Further, structure characterization was carried out by TEM equipped with the FFT setup. Figure 3(a) shows the low magnification TEM image of the CuO nanoslice grown in the sphere-shaped structures. The CuO nanoslices are clearly evident from this image. The corresponding FFT pattern obtained from the shown nanoslices confirmed that the synthesized products are single crystalline. Figure 3(b) shows the high resolution TEM (HRSEM) image of nanoslices. The lattice spacing of 0.25 nm corresponds to the d spacing of [110] crystal planes. The corresponding FFT pattern (inset in figure 3(b)) is consistent with the HRTEM observation.

A two-tiered organization of crystallites is revealed. The CuO microspheres are, in fact, built from small crystal strips that contain even smaller one-dimensional nanoslices. These crystal slices are aligned perpendicularly to the spherical surface, pointing toward a common centre. Remarkably, as shown in figure 4, the size of the sphere is about one-eighth.

4. Conclusions

Nanostructured CuO microspheres have been fabricated through a simple solution process; these microspheres were built up with nanosticks of 80–100 nm in thickness. We believe that the present approach is a simple one for prac-

tical application. In addition, this simple and low-cost method is expected to allow large-scale production of other oxides with controllable morphologies, which is advantageous for practical application.

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