

Preparation of CuO Hollow Spheres by Oxidation of Cu Microspheres

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Copper oxide (CuO) is a p-type semiconductor with narrow band-gap of 1.2 eV and is widely used as a photoconductive material, and in gas sensors and heterogeneous catalysts.¹⁻³ Various morphologies of CuO, such as rods, wires, ribbons, spheres, and even dandelions have been obtained via different synthesis routes.⁴⁻¹⁰ Hollow microparticle CuO structures are probably of most interest due to their potential applications as catalysts, because of their low densities and large surface areas.¹¹ Hard- and soft-templates are commonly used to fabricate hollow copper oxides structures.¹²⁻¹⁵ Hollow CuO microspheres have been prepared hydrothermally from copper acetate as a precursor, and by a hydrothermal reaction using a copper-complex, in which hexamethyltriethylenetetramine (HMTA) was used as a complexing reagent.^{16,17} Dandelion-like CuO hollow microparticles were also produced, *via* a donut-like intermediate assembly that consisted of equatorial stacks of rhombic CuO strips, by hydrothermal reaction between copper nitrate and NaOH.⁸ The simplest method of making CuO is by the direct oxidation of copper metal in air. Many research groups have prepared CuO nanowires and nanotubes by oxidizing copper nanowires and foils.^{5,18-20} However, it is difficult to obtain copper metal microspheres for the preparation of hollow CuO microspheres by direct thermal oxidation. Here, we describe a straightforward method for preparing hollow CuO microspheres with radially projecting surface nanorods via the direct thermal oxidation of copper metal microspheres. The morphologies of CuO microspheres and the mechanism of their formation are discussed.

Experimental Section

CuCl₂·2H₂O (99%, Aldrich), triethylenetetramine (TETA, 98%, TCI), cyclohexane (98%, Aldrich), glucose (99.5%, Aldrich) and cetyltrimethylammonium bromide (95%, CTAB, TCI) were used as received. The method used to synthesize copper metal microspheres has been described previously.²¹ To synthesize copper metal microspheres, 8 mmol of TETA and 8 mmol of glucose were added to 20 mL of a 0.2 M CuCl₂ aqueous solution with stirring, and then 1.6 g of CTAB and 40 mL of cyclohexane were added. This mixture was then transferred to a 100 mL Teflon-lined autoclave and heated at 120 °C for 24 h. After the reaction was complete, the product was filtered, washed several times with ethanol, and dried at 60 °C for 12 h. Hollow CuO microspheres were prepared by simply heating the copper metal microspheres in air for 5 h. In the present study, copper microspheres were placed in an alumina

crucible and heated to the indicated temperatures in a box-type furnace.

The structures of the copper metal microspheres and the hollow CuO microspheres were analyzed by powder X-ray diffraction (XRD, PANalytical, X'pert PRO MPD) using Cu K α 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(A) shows an SEM image of copper metal microparticles prepared by the reductive hydrothermal reaction of copper-TETA complex using CTAB as a soft template and glucose as a reducing agent. The microparticles obtained were remarkably uniform and spherical in appearance of average diameter 1 μ m. Figure 2(A) shows the XRD pattern of these copper metal particles. All XRD peaks were assigned to the cubic phase of copper metal and coincided with literature values (JCPDS 04-0836, $a = 3.6150$ Å). Moreover, no other peaks were detected, indicating that the copper metal was relatively pure. TETA was used as a tetradentate ligand during the synthesis. TETA reacts with the copper ion to form a stable copper-amine complex [Cu(TETA)]²⁺, which reacts with OH⁻ in basic solution to form copper metal due to reduction by glucose under hydrothermal conditions. The spherical morphology of copper metals is due to the presence of CTAB, which acts as a surfactant. The possible chemical reaction producing the copper metal microparticles is:

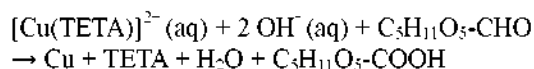


Figure 1 (B-E) shows SEM images of the hollow CuO microparticles prepared by the direct thermal oxidation of copper metal microparticles in air at temperatures between 300 °C and 600 °C for 5 h. At 300 °C, radially orientated nanorods formed on the surfaces of the hollow microparticles. The nanorods were about 20 nm wide and up to 0.5 μ m long. It was also noted the nanorods that formed on the surfaces of the copper oxide microparticles at 400 °C were shorter and thicker than those that formed at 300 °C. At 500 °C and 600 °C, the hollow spheres sintered to form aggregates.

Figure 2 (B-E) shows the XRD patterns of products obtained by oxidizing copper metals at temperatures from 300 °C to

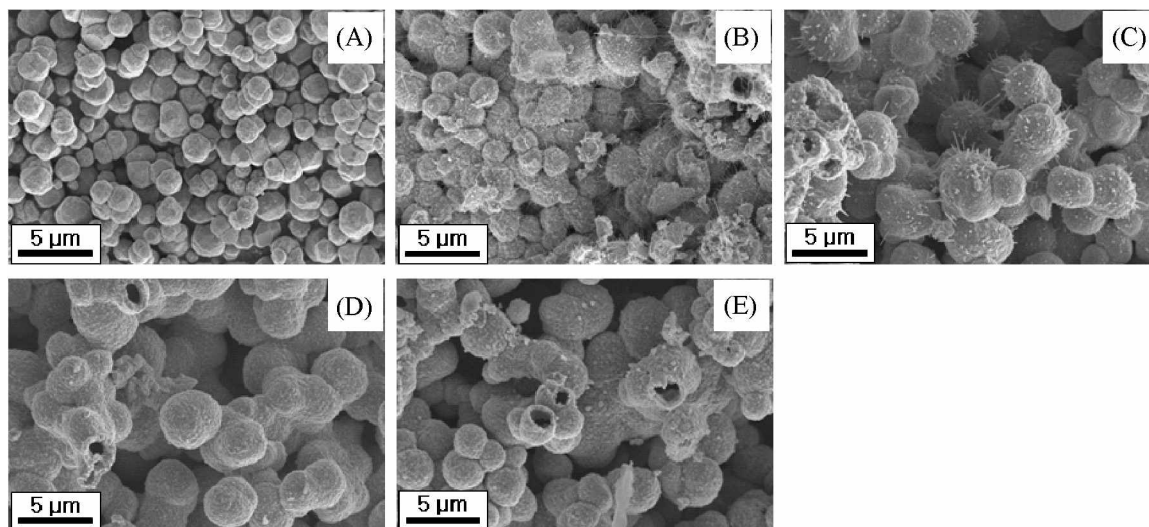


Figure 1. SEM image of (A) spherical copper metals produced using a reductive hydrothermal reaction of copper-TETA complex. (B, C, D, and E) SEM images of hollow CuO microspheres prepared by heating copper metals in air at (B) 300 °C, (C) 400 °C, (D) 500 °C, and (E) 600 °C.

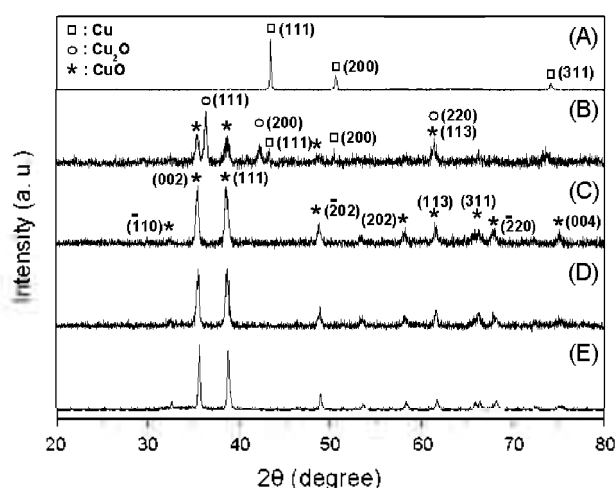


Figure 2. X-ray diffraction patterns of (A) spherical copper metals and (B, C, D, and E) CuO microspheres prepared by heating copper metals in air at (B) 300 °C, (C) 400 °C, (D) 500 °C, and (E) 600 °C.

600 °C. At 300 °C, most of the peaks observed matched to those of Cu₂O, other minor peaks were attributed to Cu₂O and Cu, as shown in Figure 2(B). Observed CuO peaks matched those of monoclinic CuO (JCPDS 45-0937, $a = 4.6853 \text{ \AA}$, $b = 3.4257 \text{ \AA}$, $c = 5.1303 \text{ \AA}$, $\beta = 99.549^\circ$) and cubic Cu₂O (JCPDS 05-0667, $a = 4.2696 \text{ \AA}$), respectively. At above 400 °C, XRD patterns indicated that pure CuO was obtained. Based on XRD findings, we suggest that Cu metals are initially oxidized to Cu₂O and that CuO is formed by further oxidation.

Figure 3(A) shows an SEM image of CuO nanorods on surfaces of hollow copper oxide microspheres. Figure 3(B) and 3(C) are TEM images taken at different magnifications of these CuO nanorods. The lengths and widths of nanorods were *ca.* 400 nm and 20 nm, respectively. Figure 3(D) shows a high-resolution TEM (HRTEM) image of a CuO nanorod. Fringe patterns indicated a spacing of 2.32 Å, which corresponds to the (111) plane of CuO.

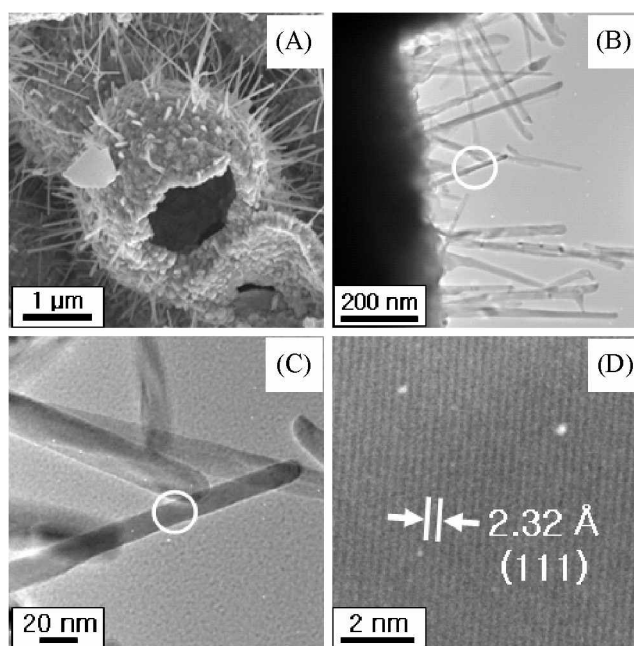


Figure 3. (A) SEM, (B, C) TEM, and (D) HRTEM images of hollow CuO microspheres with surface nanorods produced by the oxidation of copper metals in air at 300 °C with different magnifications.

The Cu to CuO oxidation was investigated by SEM, TEM, and XRD. Our observations suggest that the hollow CuO microsphere structure was formed by copper vapor diffusion. The copper vapors move outside of the surface of spherical copper metal microparticles, and react with the oxygen in air to produce the copper oxides. Accordingly, it appears that CuO formation is associated with the diffusion of copper from within copper spheres to their surfaces to form Cu₂O initially and finally CuO. Thus, the reaction appears to proceed via the diffusion of copper vapor with Fick's first law. This might be a sort of the Kirkendall effect.²² At intermediate temperatures of 300 °C and 400 °C, the diffusion rate of copper appears

moderate, and the CuO particle formed acts as a seed for CuO nanorod formation. The microspheres of copper metals were formed by aggregation of nanoparticles of copper metals as shown in Figure 1(A). The surfaces of the spherical copper metals have tiny hole, the copper vapors can diffuse through the hole. When the diffusion rate of copper is moderate, only small amounts of copper vapor diffuse through the hole in one direction. Thus, CuO nanorods were formed from the CuO seed at the hole as shown in Figure 3(A). However, the CuO nanorods formed at 400 °C were shorter than those formed at 300 °C, which suggests that they are formed during relatively mild conditions. The copper vapors move effectively to outside of the microsphere and react with oxygen to produce the hollow structures of CuO without surface nanorods at 500 °C and 600 °C.

In conclusion, uniform spherical copper metals were prepared using a hydrothermal reaction between CuCl₂ in aqueous solution and glucose in a CTAB/TETA/water/cyclohexane reaction system, in which CTAB was used as a soft template and glucose as a reducing agent. Hollow spherical CuO microspheres were obtained by simple thermal oxidation at temperatures ranging from 300 °C to 600 °C in air. Furthermore, CuO nanorods were observed on the surfaces of CuO microparticles produced at 300 °C. We suggest that the formation of these hollow spherical and nanorod structures is due to the diffusion of copper vapors from within copper metal microparticles to their surfaces.

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