

Fabrication of Hierarchical CuO Microspheres

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Hierarchical microstructures of metal oxides comprised of nanoparticles, nanorods, and nanobelts as building blocks have been attracted great interests due to their novel structures, properties, and applications.¹⁻⁷ In most systems, hierarchical assembly involves two distinct steps: 1) synthesizing the appropriate precursors, and 2) assembling them into larger structures. Copper oxide (CuO) is a narrow band-gap semiconducting oxide that has been widely used in electrochemical cells, in photothermal and photoconductive materials, and as a heterogeneous catalyst.⁸⁻¹⁰ Various techniques have been used to synthesize CuO nanostructures such as nanoparticles, nanorods, nanobelts, nanoribbons and nanotubes.¹¹⁻¹⁹ However, the methods for fabricating CuO hierarchical microstructures were examined by a few groups. Dandelion-like CuO hollow microspheres have been synthesized by a solvothermal process.²⁰ CuO microspheres have been generated by a simple solution method using sodium tartrate as a chelating agent and CuO whisker assemblies have been fabricated using a microwave-induced polyol process.^{21,22} Here we report a simple method for fabricating hierarchical CuO microspheres with an average diameter of 1.5-2.5 μm under the microwave irradiation. In this method, the CuO microspheres are built from small flakes, each comprised of several nanoplates of 15-25 nm wide and about 400 nm long. The effect of capping reagent concentration on the morphologies of the CuO products was also investigated.

Experimental Section

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich) and N,N,N',N' -tetramethylethylenediamine (TMEDA, Aldrich) were used as received. TMEDA was used as the capping reagent. In a typical procedure, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2 mmol) and TMEDA (4, 6, 8, or 10 mmol) were dissolved in 100 mL of water, and then 50 mL of 0.1 M NaOH aqueous solution was added. The mixed solution was then placed in a domestic microwave oven (Amana M84T, 2.45 GHz, 25 W) in air, and irradiated for 2 h using 100% of the output power of the microwave oven. The products were centrifuged and washed with water and ethanol several times, and then dried at 60 °C for 12 h in an oven. To investigate the effect of microwave irradiation period, the mixed solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2 mmol) and TMEDA (10 mmol) in 100 mL of water, and 50 mL of 0.1 M NaOH was irradiated for 10 min, 30 min, 1 h, and 2 h.

The aqueous mixtures of 100 mL of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2 mmol) and TMEDA (10 mmol) and 50 mL of NaOH (0.05, 0.10, 0.20, or 0.40 M) were irradiated for 2 h to examine the effect of NaOH concentration for the formation of CuO microsphere.

The structures of the CuO microspheres were analyzed by powder X-ray diffraction (XRD, Rigaku DMAX-III A) using Cu K_α radiation, and the morphologies of the hierarchical assemblies of CuO microspheres were characterized by scanning electron microscopy (SEM, Hitachi S-4300) and transmission electron microscopy (TEM, JEOL 2100F).

Results and Discussion

Figure 1 shows the XRD pattern and Miller indices of the CuO products obtained from an aqueous mixture of 100 mL of 0.02 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.10 M TMEDA and 50 mL of 0.1 M NaOH under the microwave irradiation. All of the peaks could be assigned to the monoclinic phase of CuO and coincided with literature data (JCPDS 45-0937, $a = 4.6837 \text{ \AA}$, $b = 3.4226 \text{ \AA}$, $c = 5.1288 \text{ \AA}$, $\beta = 99.54^\circ$).²³ No other peaks were detected, indicating that this simple method under microwave irradiation yielded CuO free from impurities.

The overall morphologies of the products were examined by SEM and TEM. Figure 2 shows SEM micrographs of the CuO products obtained using different concentrations of

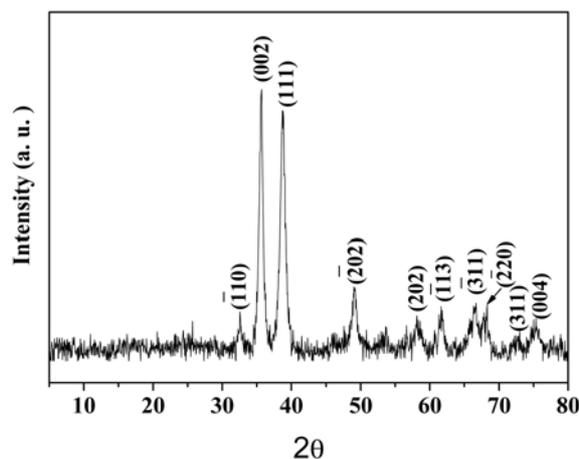


Figure 1. XRD pattern and Miller indices of the as-synthesized hierarchical CuO microspheres.

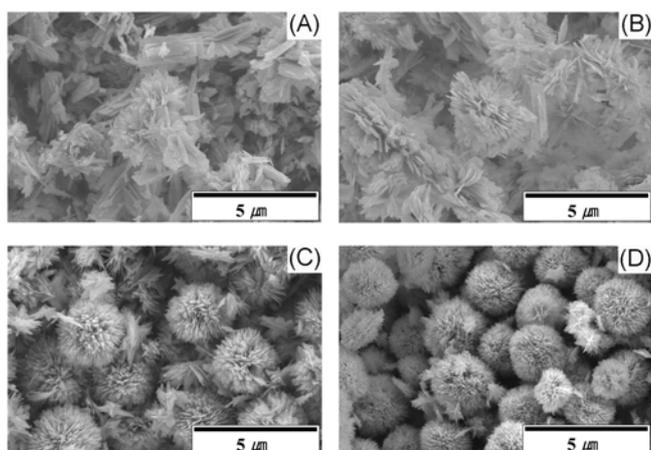


Figure 2. SEM images of the as-synthesized hierarchical CuO products obtained using different concentrations of TMEDA: (a) 0.04 M, (b) 0.06 M, (c) 0.08 M, and (d) 0.10 M.

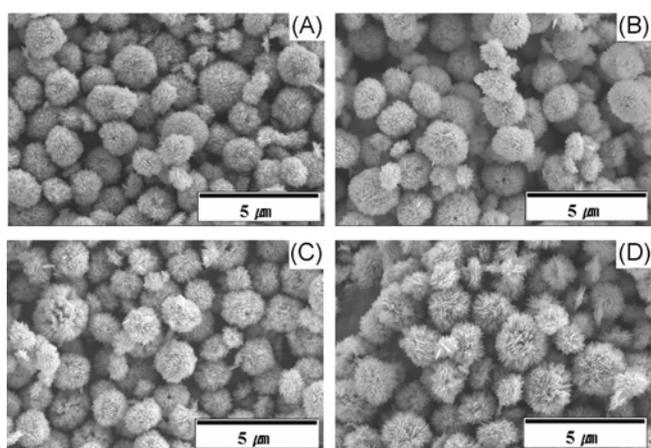


Figure 3. SEM images of the CuO products obtained with 0.10 M TMEDA for various microwave irradiation periods: (a) 10 min, (b) 30 min, (c) 1 hr, and (d) 2 hr.

TMEDA. As the concentration of TMEDA increases, the morphology of the CuO products changes from simple aggregated flakes to spherical assemblies. At lower concentrations of TMEDA, neighboring CuO flakes aggregate with a face to face configuration. At higher TMEDA concentrations, the CuO flakes are assembled into microspheres. The external shape of the CuO products obtained with 0.10 M TMEDA resembles a chestnut bur. Since we did not use any surfactants, the CuO microspheres were formed by self assembly of the CuO flakes. From the SEM micrographs, the CuO flakes were found to be about 250 nm wide and up to 1 μm long, with thicknesses of less than 50 nm. At the highest TMEDA concentration examined (0.10 M, Figure 2(d)), the flakes are aligned toward the center of a sphere to form concentric hierarchical assemblies with a spherical shape. The tendency to form spheres may be due to the driving to minimize the geometric surface energy.

Figure 3 shows SEM micrographs of the CuO products obtained with 0.10 M TMEDA for various microwave irradiation periods. The reaction mixture gradually turned

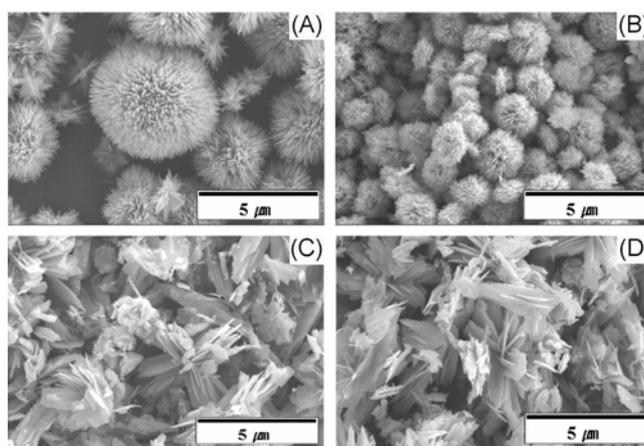
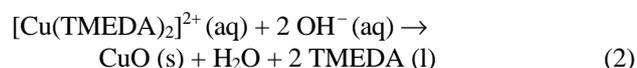


Figure 4. SEM images of the CuO products obtained with 0.10 M TMEDA using different concentrations of NaOH: (a) 0.05 M, (b) 0.10 M, (c) 0.20 M, and (d) 0.40 M.

into black over the 10 min of microwave irradiation. The morphology and size of CuO products did not show significant change with various microwave irradiation periods. The CuO microspheres did not grow more by additional microwave irradiation. Figure 4 shows SEM micrographs of the CuO products obtained using different concentrations of NaOH. Below the 0.10 M NaOH, the morphologies of the CuO products resemble the chestnut bur-like. The size of the CuO product obtained in 0.05 M NaOH is much larger than that in 0.10 M NaOH. Above the 0.20 M NaOH concentrations, the CuO flakes do not assemble to form the microspheres.

The TMEDA and NaOH play important roles in the formation of the CuO flakes in the present work. TMEDA is a water-soluble and bidentate amine that can combine with Cu^{2+} to form a $[\text{Cu}(\text{TMEDA})_2]^{2+}$ complex. This complex reacts with OH^- in solution under microwave irradiation to form CuO via the release of TMEDA in conjunction with dehydration. The possible chemical reactions of producing CuO are as follows:



The CuO microspheres are easily formed with lower NaOH concentration and higher TMEDA concentration. The rate of reaction (2) will increase with the NaOH concentration. There is not enough time to form the self-assembled CuO microspheres at higher NaOH concentrations. The CuO products above 0.20 M NaOH show only flake morphologies. The concentration of TMEDA affects also the reaction rate to formation of CuO. Cu^{2+} will directly react with OH^- to form CuO rapidly without TMEDA. TMEDA reacts with Cu^{2+} to form the $[\text{Cu}(\text{TMEDA})_2]^{2+}$ complex. It retards the reaction rate and has an enough time to assemble the flake to form the microspheres. Therefore, the rate of reaction (2) should be decreased to form the self assembled

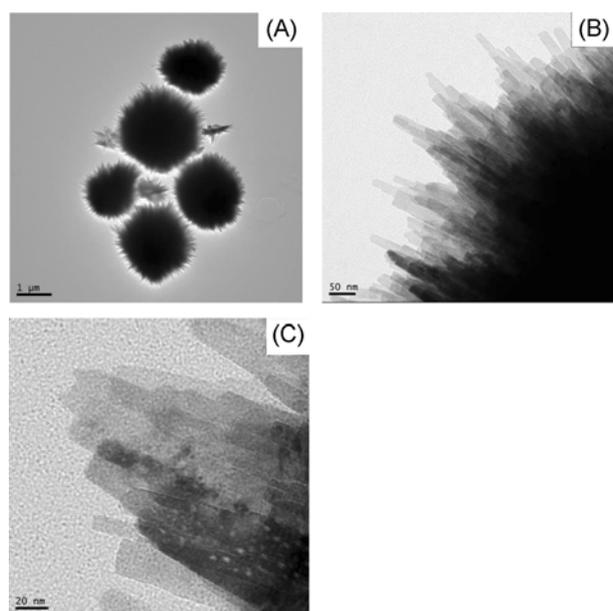


Figure 5. TEM images of the as-synthesized hierarchical CuO products obtained using 0.10 M TMEDA: (a) individual microsphere, (b) and (c) detailed structures assembled by CuO nanoplates at different magnifications.

CuO microspheres.

Figure 5 shows TEM images of the hierarchical CuO microspheres synthesized with 0.10 M TMEDA. The chestnut bur-like CuO microspheres are composed of hundreds of flakes and have an average diameter of 1.5–2.5 μm . Figures 5(b) and 5(c) show TEM images of the tip of a chestnut bur-like CuO microsphere recorded at different magnifications. These images reveal the presence of nanoplates of width 15–25 nm which, similar to the flakes, are predominantly aligned toward the center of the sphere. Figure 6 shows an HRTEM image of a single CuO nanoplate of about 25 nm wide. The inset fringe pattern of the single CuO nanoplate indicate that the distance spacing is 2.45 Å, corresponding to the (002) plane of CuO. These TEM findings thus indicate that the CuO flakes observed in the SEM images (Figure 2) are each comprised of dozens of nanoplates with widths of 15–25 nm with the same alignment.

The overall shape of the hierarchical assemblies of CuO microspheres synthesized in the present work is similar to that of the Dandelion-like CuO hollow microspheres synthesized by Liu and Zeng.²⁰ Hence, the hierarchical assemblies of CuO microspheres reported here may have formed via a mechanism similar to that suggested by Liu and Zeng. Specifically, the hierarchical assemblies of CuO microspheres may have formed via a two-step mechanism, in which dozens of nanoplates of about 25 nm wide first aggregate to form flakes of 250 nm in width and up to 1 μm in length, and then the flakes assemble into microspheres of diameter 1.5–2.5 μm . However, the shape and size of the flakes in the CuO microspheres synthesized in the present work differ from those of the crystal strips in the Dandelion-like CuO hollow microspheres synthesized by Liu and Zeng. In

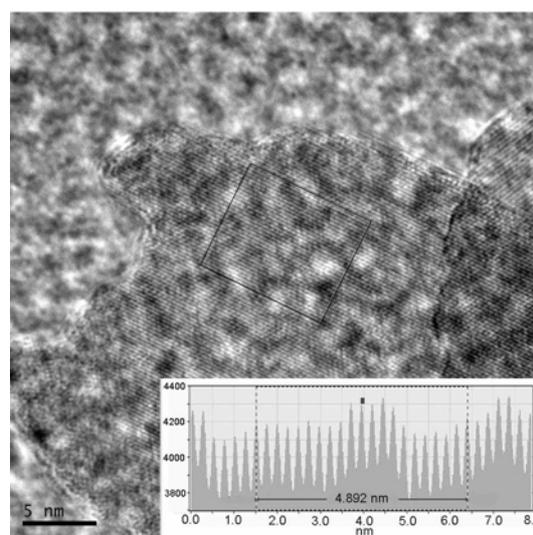


Figure 6. HRTEM image of the tip of a CuO nanoplate. The inset shows fringe patterns of the indicated area.

particular, Liu and Zeng obtained microspheres with diameters of 4 to 8 μm , which is substantially larger than the diameters obtained using the method described here. Moreover, the SEM images reveal that the CuO microspheres synthesized in the present work are not hollow (Figure 2(a) and 2(b)). Liu and Zeng fabricated their microspheres using a Teflon-lined stainless steel autoclave at 100 $^{\circ}\text{C}$ for 24 h. Zhao *et al.* also obtained assembled CuO as well as Cu₂O and Cu metal with different morphologies such as cube, sphere, and whisker. They used copper acetate and ethylene glycol under microwave reflux system. The formation of CuO depends strongly on the amount of ethylene glycol. The CuO products were assembled whiskers with diameter of 200 to 500 nm, which is not monodispersed. They are much smaller than the diameters obtained by our method. Xu *et al.* fabricated CuO prickly microsphere by using sodium tartrate as a chelating agent. Hydrothermal reaction was carried out by using Teflon-lined autoclave at 180 $^{\circ}\text{C}$. They fabricated different sizes of CuO by controlling the molar ratio of NaOH to copper ion. The CuO products have the aggregated form of microspheres. However, we employed a simple solution method using a domestic microwave oven at room temperature. Our simple method is therefore more amenable to the large-scale fabrication of monodisperse CuO microspheres.

In conclusion, we synthesized CuO microspheres with an average diameter of 1.5–2.5 μm under microwave irradiation. These microspheres were formed via the assembly of flakes of 250 nm in width and up to 1 μm in length, each of which was formed by the assembly of dozens of smaller nanoplates with widths of about 25 nm. As the concentration of TMEDA was increased and the concentration of NaOH was decreased the morphology of the CuO products changed from simple aggregated flakes to spherical assemblies. The external shape of the hierarchical CuO microspheres resembled a chestnut bur.

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