Mesoscale Organization of CuO Nanoribbons: Formation of "Dandelions"

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Over the past several years, large-scale self-assembly of meso-, micro-, and nanostructured building components has attracted significant interest in materials synthesis and device fabrications.[1-14] A number of self-assembly processes, based on different driving mechanisms, have been available. For example, surface tension, capillary effects, electric and magnetic forces, and hydrophobic interactions have been utilized in various organization schemes.[1-14] In addition to common one-, two-, and three-dimensional architectures,[1-12] controlled organization of primary building units into curved structures represents another challenge for materials self-assembly, as hollow structures (e.g., tubular, spherical) are highly demanded in new technological applications.[15-17] Regarding generation of curved architectures from prefabricated components, two approaches have been developed.[13,14] The first method has fabricated "colloidosomes" in which emulsified droplets act as soft templates for self-assembly of colloidal particles (i.e., polymeric beads) into elastic spherical shells.[13] The second one, on the other hand, has successfully examined control factors to organize artificial building blocks (i.e., one-dimensional organic–inorganic hybrid rods) into various curved single-layer superstructures.[14] In this communication, we report another scheme for the generation of curved architectures with in situ formed building blocks at the following organizing steps: (1) nanoribbons of CuO spontaneously attached into rhombic crystal strips and (2) the in situ formed building units from (1) then self-assembled into dandelion-like architectures with hollow interiors. This one-pot hierarchical organizing scheme relies primarily on geometric constraints of building blocks, which is different from the reported schemes that employed either emulsified soft templates or hydrophobic attraction that resulted from variation of the chemical composition of the building units.[13,14]

The starting solution of copper (1.00 M) was prepared by mixing $Cu(NO_3)_2 \cdot 3H_2O$ in pure ethanol solvent. Typically, 15–25 mL of the above solution was added with 15–25 mL of ammonia solution (32%), followed by an addition of 4–5 mL of aqueous NaOH (1.00 M) and 0–5 g of solid $NaNO_3$. The solution mixture was transferred to a Teflon-lined stainless steel autoclave which was then heated at 100–180 °C for 2–24 h in an electric oven. After reaction, the autoclave was cooled in tap water, and CuO products were washed via centrifugation–redispersion cycles, with each successive supernatant being decanted and replaced with deionized water and ethanol. The crystallographic information was established with powder X-ray diffraction (XRD, Shimadzu XRD-6000, Cu Kα radiation). The dimension, morphology, crystal lattice, and composition of the obtained CuO samples were characterized with scanning electron microscopy (SEM, JSM-5600LV), field-emission SEM (FESEM, JSM-6700F), transmission electron microscopy and selected area electron diffraction (TEM/SAED, JEM-2010F, 200 kV), and high-resolution transmission electron microscopy and energy-dispersive X-ray spectroscopy (HRTEM/EDX, Philips-CM200 FEG, 200 kV). Specific surface areas of CuO samples were also measured by the BET method (NOVA-3000).
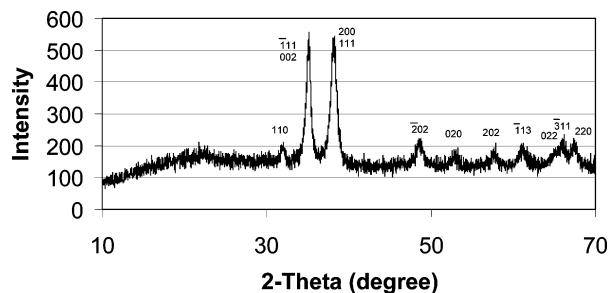

Figure 1. A representative XRD pattern recorded for CuO microspheres synthesized in this work.
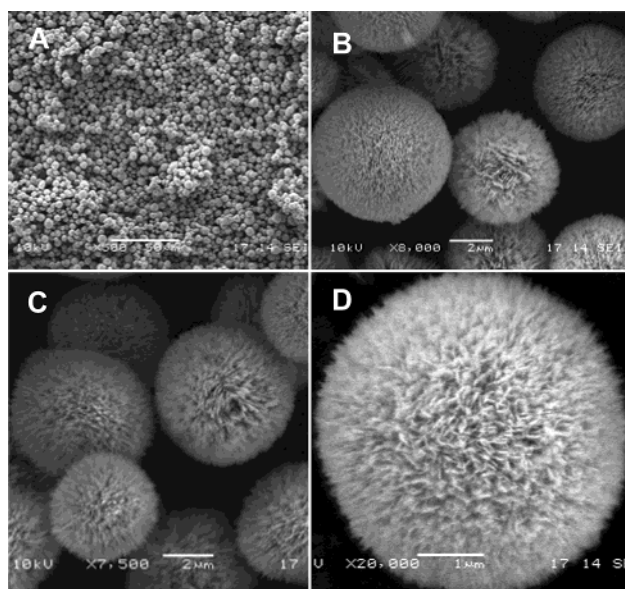

Figure 2. SEM images of CuO microspheres (prepared at 100 °C, 24 h): (A) overall product morphology; (B and C) detailed views on average-sized spheres; and (D) a detailed view on an individual sphere.

The structure and chemical composition of all CuO samples synthesized in this work were confirmed with XRD and EDX methods. As reported in Figure 1, the XRD diffraction peaks are rather broad, indicating the nanocrystalline nature of the synthesized samples. All recorded peaks can be assigned to the monoclinic symmetry of this oxide (SG: $C2/c$; $a_o = 4.684$ Å, $b_o = 3.425$ Å, $c_o = 5.129$ Å, $\beta = 99.47°$; JCPDS file no. 05-0661).[18] Consistent with the XRD results, the EDX method also reveals that the atomic ratio of Cu to O in our samples is equal to 1:1 (Supporting Information (SI)-1).

Figure 2 shows general morphologies of the as-prepared CuO samples. Interestingly, the CuO crystallites self-organized into spherical assemblies or "dandelions" with a puffy appearance. Under the reported conditions, the CuO products are all in this morphology (100%), with diameters ranging from 4 to 8 μm.
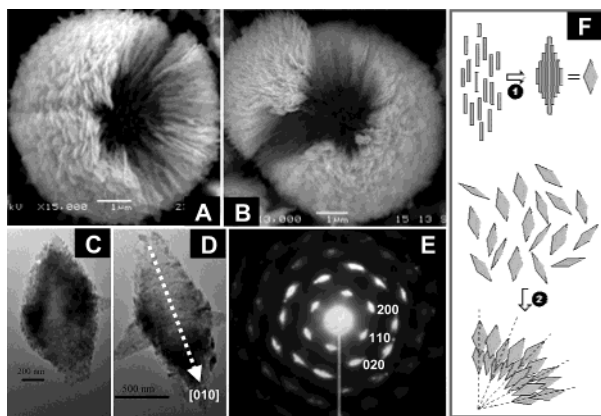
Figure 3. (A and B) SEM images of two crashed CuO microspheres; (C and D) TEM images of two rhombic CuO crystal strips formed from smaller one-dimensional nanoribbons; (E) SAED pattern ([001] zone) of the crystal strip shown in (D); and (F) Two-tier organization with multiple-length scales: (1) oriented aggregation of CuO nanoribbons, and (2) concentric alignment of the preformed rhombic building blocks from (1).

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 nanoribbons. These crystal strips, analogous to the "parachutes" in a dandelion, are aligned perpendicularly to the spherical surface, pointing toward a common center. Remarkably, as shown in Figure 3, the "dandelions" are coreless with a hollow cavity. The thickness of the shell wall is about one-third to one-quarter of the sphere diameter. The feathery shell comprises loosely packed crystal strips, having communicable intercrystal space to its central interior (SI-2). In agreement, large specific surface areas of the as-prepared CuO spheres in the range of $50-60$ m^3/g were determined in our BET measurements, depending on the synthetic conditions. Similar CuO microspheres can also be prepared in 100% morphological yield at temperatures below 100 °C (e.g., 60 or 80 °C; SI-3). In general, lower temperatures tend to generate more finely sized CuO crystal strips. Other synthetic parameters have also been examined. For example, it has been revealed that adding common inorganic salts such as NaNO$_3$ does not show additional effects on the product morphology, noting that high electrolyte concentrations had already been adopted in our general synthesis.

Formation of free-standing CuO nanoribbons had been studied in an earlier work.[18] Our SEM/TEM/SAED investigation in Figure 3 indicates that the nanoribbons that construct the rhombic CuO crystal strips (Figure 3C and D) have breadths of about $10-20$ nm and lengths not exceeding the strip dimension in [010] (HRTEM/TEM, SI-4). The nanoribbons are aligned with one another along some main crystallographic axes of CuO via an "oriented attachment" process,[19–21] as elucidated in Figure 3E which shows that the overall assembly is essentially single crystalline. The dimension of CuO crystal strips has the following hierarchical order [010] > [100] ≫ [001],[18] while the thickness of the crystal strips in [001] is $20-30$ nm (by FESEM, SI-2). The easy detection of crystal lattice fringes of d_{110} (2.7 ± 0.1 Å) and d_{200} (2.3 ± 0.1 Å) along the CuO nanoribbons in the rhombic crystalline building blocks further confirms this observation (HRTEM, SI-4).

Regarding the formation of spherical structure, the geometrical shape of building blocks must have played a key role, since no surfactants/emulsions were used. A simple array of rhombic CuO crystal strips will easily generate a curvature, and the lateral engagement of these building units would naturally lead to a shell structure depicted in Figure 3F. Consistent with this model, it is observed that the interior surface of the spheres is more compact than the exterior surface (SI-5). Our time-dependent experiments indeed agree with the above assembly mechanism (at 100 °C, SI-6). Under the present synthetic conditions, bundles of CuO crystal strips were readily formed after a short reaction time (1 h; SI-6). With a longer reaction time, the CuO crystal strips were gradually organized into microspheres (4 and 12 h; SI-6). Quite interestingly, the final spherical structure was actually formed through a donut-like intermediate that consists of equatorial stacks of CuO crystal strips (SI-7). The interconnect bonding among the crystal strips is strong. As tested, only a small degree of surface disintegration was observed after a prolonged sonication (SI-8). Interpenetration among the CuO spheres has also been observed, where exterior openness is responsible for this external bonding capacity when mobility of the microspheres is low during the synthesis (SI-9). As an extension, our preliminary investigation on other metal oxides shows that similar hierarchical organizations for spherical morphology could also be attained by introducing geometric constraints to primary structural units.[22]

In summary, a two-tiered organizing scheme for construction of CuO microspheres with interior space has been elucidated: (1) mesoscale formation of rhombic building units from smaller nanoribbons via oriented aggregation and (2) macroscopic organization of these units into the CuO microspheres. This self-assembly concept may also be applicable to other metal oxides by creating geometric constraints for constructional units.

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