Hollow ZnO Microspheres with Complex Nanobuilding Units

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Over the past decade, hollow structures have received great attention in the general synthesis of functional materials because of their important applications in vastly different fields.[1–6] Among known preparative methods,[1–6] templating has been proven to be an effective approach to tailor-make interior spaces of hollow structures, in which both hard templates such as inorganic or organic core supports and soft templates such as vesicles and micelles in emulsions or ionic liquids have been utilized.[1–4] To explore new capabilities of templating method, researchers should further investigate the self-assembly of nanobuilding units on the interface or surface of the templates, because it belongs to the general "bottom-up" paradigm adopted in nanotechnology.[2] In particular, several types of colloidosomes assembled from sphereical or rodlike polymeric building blocks have been fabricated with colloidal templating.[2] It is noted, however, that in these pioneering works, the constructional units are limited to only simple geometrical shapes.[2] Herein, we will use zinc oxide (ZnO, an important electronic and photonic material with a direct band gap of 3.37 eV [7]) to demonstrate that hollow spheres of metal oxides with external diameters up to several tens of micrometers can be prepared via assembly of complex nanobuilding units, which, in turn, were constructed from even smaller unidirectionally attached nanorods.

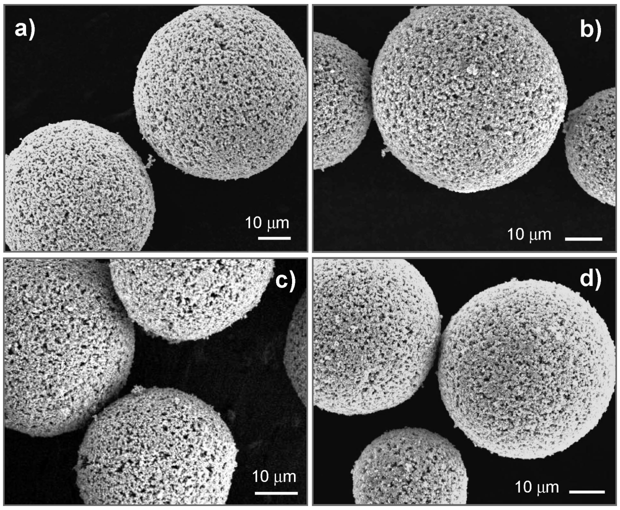

Figure 1. SEM images of hollow ZnO microspheres assembled from numerous complex nanobuilding units (also see Figure 3): (a–c) 100 °C for 2 h, and (d) 80 °C for 2 h (see the Supporting Information, SI-1, for more experimental details).

In our synthesis, 0.5−1.0 g of cetyl-trimethyl-ammonium-bromide (CTAB) was dissolved in 30.0−60.0 mL of pure ethanol under vigorous stirring. The CTAB-containing ethanol solution became clear and was then added to 3.0−6.0 mL of zinc nitrate solution ($Zn(NO_3)_2 \cdot 6H_2O$; $[Zn^{2+}] = 0.50$ M, $[Zn^{2+}]:[OH^-] = 1:10$), followed by adding 5.0 mL of ethylenediamine ($C_2H_4(NH_2)_2$, EDA). The solution mixture was continuously stirred for 5 min and then transferred to a Teflon-lined stainless steel autoclave and kept at 80−180 °C for 20−180 min inside an electric oven. ZnO products were collected by centrifugation and thorough washings with water. Detailed synthetic conditions for all samples reported herein can be found in the Supporting Information, SI-1. The prepared ZnO samples were further characterized with powder X-ray diffraction (XRD, Shimadzu XRD-6000, Cu Kα radiation), scanning electron microscopy, energy-dispersive X-ray spectroscopy (SEM/EDX, JSM-5600LV), field-emission SEM (FESEM/EDX, JSM-6700F), transmission electron microscopy, selected area electron diffraction (TEM/SAED, JEM-2010F, 200 kV), and high-resolution TEM (HRTEM, Philips-CM200 FEG, 200 kV). Specific surface areas of the ZnO samples were also measured with the Brunauer–Emmett–Teller method (BET, NOVA-3000).

Figure 1 shows the general morphology of ZnO spheres prepared at the optimal conditions of 80−100 °C (see the

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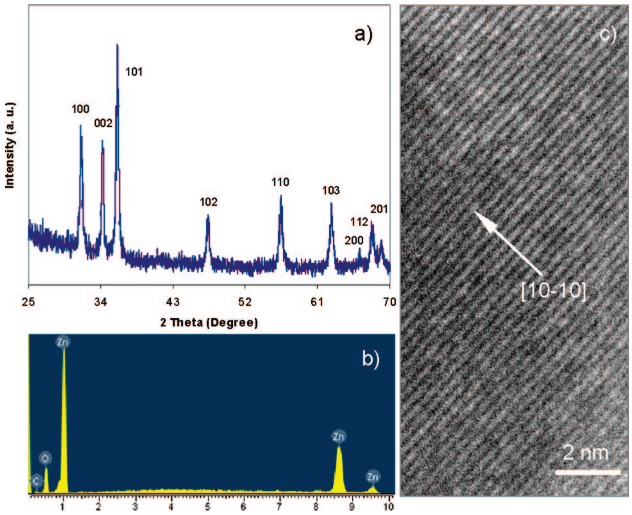

Figure 2. (a) XRD pattern, (b) EDX spectrum, and (c) HRTEM image ($d_{10-10} = 2.8 \pm 0.2$ Å) of hollow ZnO microspheres.

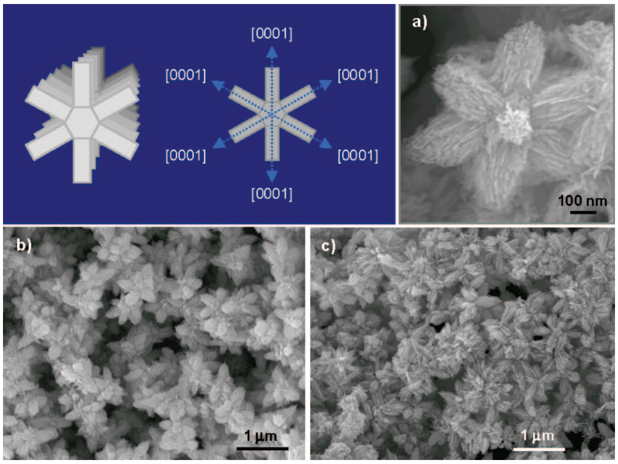

Figure 3. FESEM images of assembled nanobuilding units in ZnO microspheres: (a) the nanobuilding unit, (b) inner surface of a ZnO microsphere, and (c) outer surface of the same microsphere. Color inset indicates crystallographic orientations of the complex building units; the central stem is viewed along the [0001] axis of ZnO.

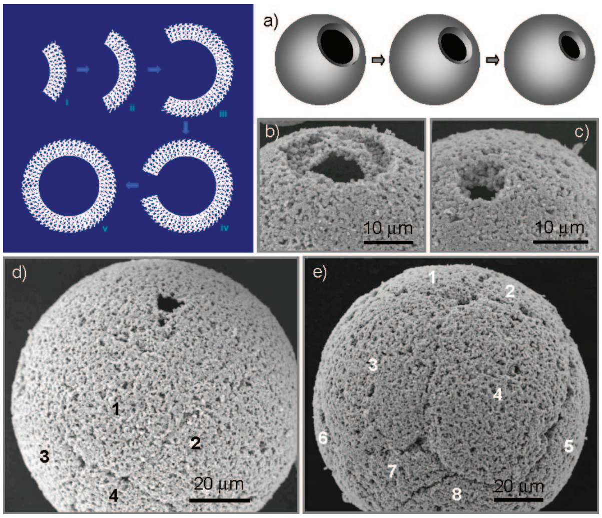

Figure 4. (a) Self-assembling process (see steps i–v of the color inset, cross-sectional view); (b, c) FESEM images of final openings of ZnO microspheres corresponding to (a); and (d, e) SEM images of domains (marked with alphabetical numbers) of assembled nanobuilding units.

Supporting Information, SI-1, for experimental parameters); the morphological yield of hollow spheres is 100%. The diameter range of the spheres is ca. 20–100 μm, and the constant shell thickness is about 3–4 μm (see the Supporting Information, SI-2). The porous nature of the spheres can be clearly seen on both interior and exterior surfaces of these hollow spheres. As reported in Figure 2, our XRD and EDX measurements further confirm that the oxides prepared in this way have a wurtzite-type phase (JCPDS card 36-1451; SG, $P6_3mc$; $c_o = 5.21$ Å and $a_o = 3.25$ Å), and a 1:1 Zn:O stoichiometric atomic ratio.[7] The specific surface area measured with the BET technique is ca. 17 m^2/g. Detailed views on the shell structure indicate that the ZnO microspheres are comprised of numerous flowerlike building units, as shown in Figure 3a. On the basis of a TEM/SAED analysis (see the Supporting Information, SI-3), it is known that each arm in this multipod unit is pointing toward its own [0001] direction, including the central stem (see color inset). More interestingly, each crystal stem or arm is formed from even smaller ZnO crystal nanorods that are “fused” together (Figure 3a and the Supporting Information, SI-3), i.e., the tiny nanorods are oriented toward the same global crystal axes in accordance with the oriented attachment mechanism.[8] The lattice fringes displayed in Figure 2c confirm that the individual ZnO stems/arms are single-crystalline (or mesocrystalline). Therefore, three tiers of organization have been found herein: (i) oriented attachment of the nanorods into central stems, (ii) formation of complex multipod units, and (iii) construction of spheres with the nanobuilding units formed in (ii). Apparently, this hierarchical organization process must be commenced from the generation of nanorods, as they are the constructional base for the multipods, which, in turn, are the complex building units for the ZnO microspheres. Also revealed in Figure 3a and the Supporting Information, SI-3, the central stem in the multipod units is generally smaller than its six hexagonally arranged coplanar arms, suggesting that the center stems were first formed and provided its six prismatic crystal planes/facets of (10−10), (01−10), (−1010), (0−110), (1−100), and (−1100) as growth platforms for branching of multipod units, noting that a constant interarm angle at 60° has been observed in all the resultant complex nanobuilding units (Figure 3a and the Supporting Information, SI-3).

It is understandable that the formation of shell structure depends on certain binding and interpenetrating among its building units. Although they can also be attained at room temperature under normal atmosphere, more uniform spheres can be prepared at 80−100 °C (Figure 1). When temperature is high (e.g., 160−180 °C), on the other hand, Ostwald ripening becomes operative;[9] that is, large crystallites are grown at the expense of smaller ones, leaving larger nanorods and larger pinholes on the shell surface (Figure 1 and the Supporting Information, SI-4). It should be mentioned that all our ZnO microspheres give almost perfect spherical shapes, even though they were built from the geometrically

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intricate and randomly assembled units (Figure 3). To understand this, an assembly process is illustrated in the inset of Figure 4. It has been known that CTAB surfactant can form colloidal vesicles in polar media (i.e., water–ethanol in our case), which act as a soft template for the self-assembly of ZnO multipod units, whereas ZnO nanorods are synthesized with the assistance of EDA chelating agent.[10] Apart from those reported in Figure 1, importantly, incomplete ZnO spheres with a circular opening can be arrested (Figure 4b–d). These structural intermediates reveal a novel assembling process that is depicted in Figure 4a. Because the shell in the opening region is already quite thick, it is recognized that the ZnO spheres are not formed via a layer-by-layer route, but through a filling process, i.e., the assembly of ZnO multipod units is primarily taking place at the shell openings (color inset, Figure 4). Consistent with this assembling mechanism, furthermore, patchlike domains of the ZnO spheres are also occasionally observed (images d and e in Figure 4). The domain distribution and boundary indicate that the integration of ZnO multipod building units indeed can occur simultaneously in several locations of the interface of a vesicle, resulting in a soccer-ball-like appearance when the process is completed, which is different from other reported templating and conversion methods for ZnO microspheres.[11]

In summary, a three-tiered organization of ZnO nano-building blocks into hollow spherical conformations has been developed. This self-assembly approach demonstrates new capacities of template-assisted synthesis in the architecture of hollow structures as well as in construction of structurally complex nanomaterials.

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Supporting Information Available: SEM, FESEM, and TEM/SAED results (PDF). This materials is available free of charge via the Internet at http://pubs.acs.org.

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