

Morphosynthesis of Hierarchical Hydrozincite with Tunable Surface Architectures and Hollow Zinc Oxide

Chenglin Yan and Dongfeng Xue*

State Key Laboratory of Fine Chemicals, Department of Materials Science and Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, People's Republic of China

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Hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) microspheres with a tunable surface architecture have been successfully synthesized via a homogeneous precipitation method under solvothermal conditions. For a smooth hydrozincite microsphere, various building blocks such as nanocubes, nanorods, and nanosheets are arranged to cover a spherical surface by concisely controlling reaction time and the volume of ethylene glycol. Hexagonal $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ with nanostep structures are also prepared without any additives. The hollow ZnO microspheres with a porous surface have been successfully fabricated via a solution-based method by the room-temperature treatment of filled $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres composed of nanocubes. A possible growth mechanism of these hollow ZnO microspheres is proposed. The similar filled ZnO microspheres can also be obtained by a direct pyrolysis of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres composed of nanocubes at 450 °C.

1. Introduction

The arrangement of micro- and nanostructured building blocks into hierarchical structures is of great interest to chemists and materials scientists.^{1,2} The direct fabrication of hierarchical nanostructures with a controlled crystalline morphology, size, and surface architecture remains a key challenge, because these structures are of great importance in determining their widely varying properties in new technological applications.^{3–8} The major step to assemble a wide range of nanostructures in a flexible manner is first to synthesize building blocks and subsequently arrange these building blocks into curved structures. Generally speaking, by concisely controlling the nucleation, growth, and followed by self-assembly, novel architectures with various surface structures can be achieved. Here, we report a large-scale synthesis of the hierarchical hydrozincite with a tunable surface architecture using zinc acetate and urea as starting reactants and ethylene glycol as the solvent. These hierarchical hydrozincite microspheres have various surface structures. For a smooth hydrozincite microsphere, various subunits such as nanocubes, nanorods, and nanosheets are arranged to cover the spherical surface.

ZnO is an attractive semiconductor with a direct band gap of 3.37 eV, which attracts much attention in tailoring its shape and size to optimize the corresponding optical properties.^{9–12} The synthesis of hollow ZnO structures is of great interest,^{13–15} because hollow structures often have widespread potential applications such as catalysts, delivery vehicles, photonic materials, and chemical and biological sensors.^{1f} In most cases, to obtain the hollow structure, the template method is usually applied. However, introducing the template into the reaction system means a more complicated process. Zinc hydroxide carbonate ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$), naturally occurring as hydrozincite, is of great interest in numerous applications and as a precursor to prepare ZnO;^{16–18} however, in no case have uniform particles with various shapes been reported. From a fundamental

viewpoint, it is highly desirable to develop total chemical syntheses, which require mild reaction conditions under low-temperature conditions. The conventional method of the pyrolysis of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and in situ conversion of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ to ZnO requires high temperature.^{16,17} In this work, a novel method of conversion of filled $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ to hollow ZnO at room temperature is proposed. The technique is exceptionally simple and does not require high temperature. In addition, the direct pyrolysis of filled hierarchical $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres results in the similar morphology of filled ZnO microspheres.

2. Experimental Section

All chemical reagents used in this experiment were of analytical grade. The detailed synthesis procedures were described as follows. $\text{Zn}(\text{CH}_3\text{COOH})_2$ (0.003–0.03 mol) and $\text{CO}(\text{NH}_2)_2$ (0.006–0.06 mol) were added to an appropriate amount of ethylene glycol (EG). The mixture solution was stirred, and the pH value of the resulting solution was adjusted to the desired value using HCl solution (1 M) or $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25 wt %) solution. Finally, the mixture solution was transferred into a 40 mL Teflon-lined autoclave. A glass coverslip with $18 \times 18 \text{ mm}^2$ (used as the substrate for harvesting samples) was fixed at the autoclave bottom. The autoclave was then filled with an appropriate amount of water up to 80% of the total volume and was kept inside an electric oven at 80–150 °C for 1–24 h. After cooling to room temperature naturally, the $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ samples covered on the glass coverslip can be collected, which were washed with deionized water and absolute ethanol several times, respectively. Finally, the sample was dried in air at 80 °C for 4 h. To succeed in converting the hierarchical $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres to both hollow and filled ZnO microspheres, the following two methods were employed. The first one was carried out by the room-temperature treatment of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ precursor in KOH aqueous solution. $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ powder (0.004–0.4 g) and of KOH (0.56–5.6 g) were added into 40 mL of distilled water in a beaker. The reaction mixture solution was left for 4–36 h at room temperature.

* To whom correspondence should be addressed. E-mail: dfxue@chem.dlut.edu.cn.

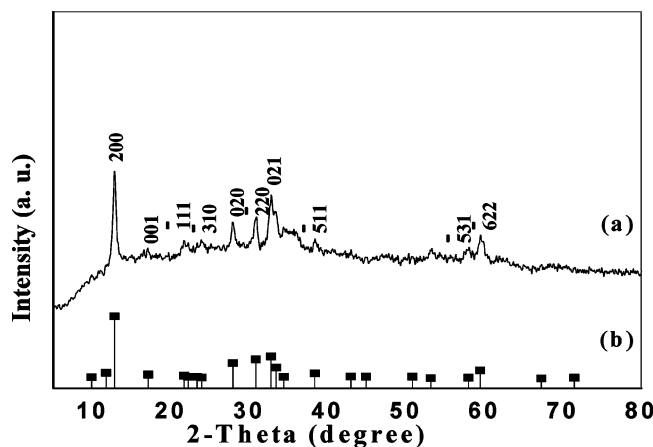


Figure 1. (a) XRD pattern of the spherical $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ with a hierarchical structure by the solvothermal reaction for 4 h. (b) Standard diffraction pattern of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ is shown as a reference.

TABLE 1: Summary of Experimental Conditions and Corresponding Surface Morphology of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$

sample no.	reaction time (h)	volume of EG ^a (mL)	surface morphology of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$
1	1.5	20	smooth surface
2	2.5	20	nanorods
3	4	20	nanocubes
4	5	20	nanocubes with a more compact surface
5	4	15	nanosheets
6	4	0	hexagonal particles

^a EG = ethylene glycol.

Finally, the ZnO precipitate was collected and washed several times with distilled water and absolute ethanol and dried at 60 °C for 4 h. In the second method, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ was transformed into filled ZnO by heating $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ at 450 °C for 3 h in air.

The as-prepared samples were characterized by an X-ray diffractometer (XRD) on a Rigaku-DMax 2400 diffractometer equipped with the graphite monochromatized Cu K α radiation flux at a scanning rate of 0.02° s⁻¹ in the 2 θ range 5–80°. Scanning electron microscopy (SEM) images were taken with a JEOL-5600LV scanning electron microscopy, using an accelerating voltage of 15 kV.

3. Results and Discussion

The purity and crystallinity of the as-prepared samples are examined using XRD. All peaks in XRD pattern of hierarchical $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres composed of nanocubes (Figure 1) can be indexed as the pure monoclinic phase of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ with lattice constants $a = 13.58$ Å, $b = 6.28$ Å, and $c = 5.41$ Å, which agree well with the reported data (JCPDS no. 19-1458). The micro- to nanostructural characteristics of the as-prepared samples are further examined by SEM. The different reaction conditions and corresponding as-prepared samples are summarized in Table 1. Figure 2 shows that the $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ particles are perfect in shape, which exhibit a hierarchical structure (Supporting Information, Figure S1) with a spherical morphology, where the secondary units are some small nanocubes. Many neighboring primary nanocubes aggregate together to form hierarchical $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres with a uniform diameter, as shown in Figure 2B. The particle diameter distribution is depicted in Figure 3. The general diameter of the as-prepared $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres composed of nanocubes falls in the range of 9.5–15.5 μm with an average

size of 15.3 μm . It is demonstrated that the surface subunit of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres can be actively controlled by adjusting the reaction time. When the reaction time is shortened to less than 1.5 h, only bare microspheres with a smooth surface are observed (Figure 4A,B). Increasing reaction time up to 2 h, the smooth microspheres begin to transform into the nanorod-assembled microspheres (Figure S2), where the smooth microspheres and nanorod-assembled microspheres are coexisted. When the reaction time reaches about 2.5 h, it can be seen from Figure 4C,D that microparticles still keep the spherical morphology, where the secondary nanorod arrays stand perpendicular to the microsphere surface. When the reaction time reaches about 3 h, the spherical surfaces start to become compact. The samples obtained in this stage shows that the microspheres evolve into the hierarchical $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ composed of nanorods. The reduction of microsphere size may be due to the fact that the nanorods coalesce and the dissolution-recrystallization process happens during this stage. Extending the reaction time to 5 h causes the more compact surface structure of microspheres (Figure 4E,F), in comparison with the hierarchical microspheres obtained at 4 h. It can be found that the change of the surface subunit and particle size of microstructures may be attributed to a dissolution–recrystallization process followed by Ostwald ripening¹⁹ under solvothermal conditions. The secondary processes during the reaction (such as the dissolution–recrystallization process and Ostwald ripening) dramatically affect the size and shape of the obtained samples.

Urea as a neutralizing agent for the homogeneous hydrolysis of aqueous solutions of some metal salts has successfully been reported.^{2a} The kinetics of nucleation and the particle growth in homogeneous solutions can be effectively adjusted by a controlled release of anions and cations. The decomposition of urea can produce hydroxide anions and carbonate anions, which form precipitates with zinc ions. OH⁻ ions are formed as a result of the reaction of H₂O with NH₃, whereas CO₂ is produced by the decomposition of urea. Subsequently, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ nuclei form rapidly. The growth speed of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ nuclei are controlled by OH⁻ and CO₂ slowly released by urea. On the other hand, for the EG reaction system, the reaction rates can be controlled through the coordination between the reactant and EG; therefore, spherical particles with a good crystallinity can be obtained. EG is employed here to protect the $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ particles from aggregation and direct the shape of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$. Due to the presence of EG during the growth of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ in solution, EG molecules are significantly adsorbed on the surface of these $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ particles, due to the fact that these $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ particles are surrounded by EG molecules, which hinder the income of fresh zinc ions and subsequently control their further growth. Furthermore, two hydroxyl groups in EG can hold free zinc ions in solution. Therefore, under the direction of these surrounding EG molecules, the special shape of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ particles with a good monodispersity can be obtained.

Our experimental results indicate that a decrease in volume or an absence of EG leads to the shape change of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ particles. When the volume of EG is decreased from 20 to 15 mL and other experimental conditions are unchanged, a SEM image in Figure 5A at low magnification shows that the densely packed and well-dispersed spherical particles with relatively uniform diameter are obtained in the presence of 15 mL of EG. An enlarged image in Figure 5B reveals that the actual surface feature of individual microspheres indicates that numerous nanosheets are self-assembled into this $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microsphere with a hierarchical structure. A decrease in

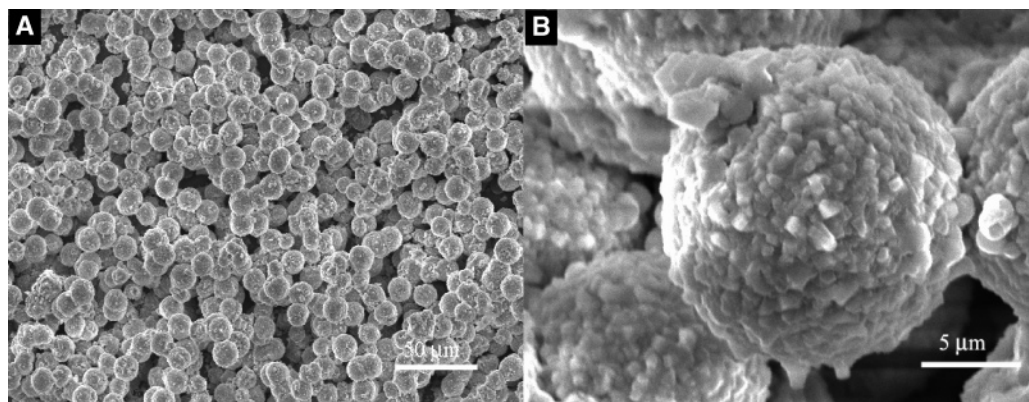


Figure 2. SEM images of the spherical $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ with a hierarchical structure composed of nanocubes by the solvothermal reaction for 4 h: (A) Panoramic morphology showing the monodispersed samples; (B) detailed view on an individual microsphere composed of nanocubes.

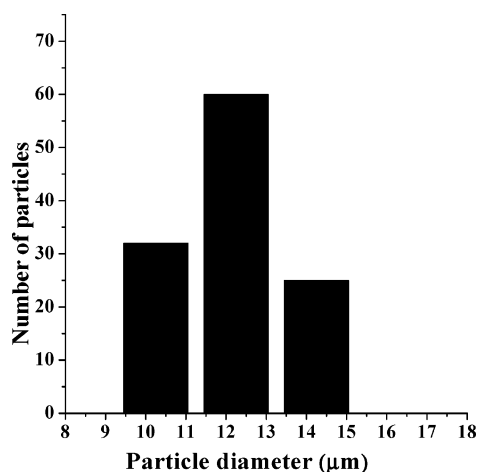


Figure 3. The diameter distribution (sample size 100 microspheres) of the spherical $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ spheres composed of nanocubes.

EG volume leads to the decrease of adsorption of EG molecular onto $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ particles, which may result in the surface subunit change of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres from nanocubes (Figure 2) to nanosheets (Figure 5A,B). Various morphologies of the samples obtained at different reaction times give us a clear evidence of the morphology transformation process (Figure S4). When the experiment is carried out without EG (keeping other experimental conditions fixed), novel hexagonal $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ particles are obtained, as shown in Figure 5C. The SEM image (Figure 5D) at high magnification shows that the tip of individual hexagonal $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ particles exhibits a sectorlike morphology. The middle section of these particles shows a uniform nanostep structure. In the viewpoint of crystallography, the shape of a single-crystalline nanostructure is often determined by the intrinsic symmetry. These novel hexagonal particles are associated with the corresponding crystallographic structure, as shown in Figure S5. Therefore, EG as a structure-template is exploited here to effectively direct the shape of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$.

It has been documented that ZnO hollow microstructures have been achieved mainly through the vapor deposition and template method. Wang et al. have reported the synthesis of hollow ZnO shells by the evaporation of ZnO, SnO_2 , and graphite powders.¹⁵ ZnO hollow structures have also been obtained by Neves et al. using ethanol droplets as templates.¹⁶ In the current work, the hollow ZnO microspheres have been successfully fabricated via a novel solution-based method by the room-temperature treatment of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres (Figure 2). To succeed in converting the filled

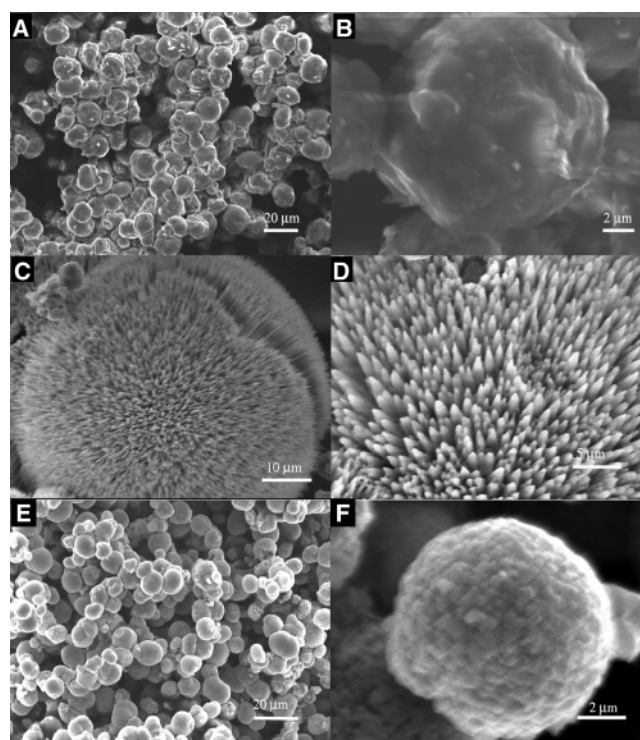


Figure 4. SEM images of the spherical $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ with various surface structures obtained at different reaction times: (A and B) Smooth surfaces at 1.5 h; (C and D) nanorod-assembled microspheres at 2.5 h; (E and F) compact surfaces at 5 h.

$\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres to hollow ZnO microspheres, the as-prepared spherical $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ powders were directly added to the KOH solution containing a higher concentration of OH^- and subsequently kept aging at room temperature. The results for the conversion of filled $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres to hollow ZnO microspheres are displayed in Figure 6. It can be observed that hollow ZnO microspheres can be formed after reaction of 4–36 h. In some parts, some broken pieces of hollow shells are observed. A high magnification image indicates that the surface of hollow microspheres shows a porous structure, as shown in Figure 6C. Therefore, our novel synthetic approach has enabled us to produce a wide range of unusual ZnO complex structures. The formation mechanism of ZnO can be easily understood by taking the following considerations. A higher concentration of OH^- may cause an increased solubility of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, which results in the fast growth of ZnO, whereas a lower concentration of OH^- could not produce ZnO. When the amount of OH^- is

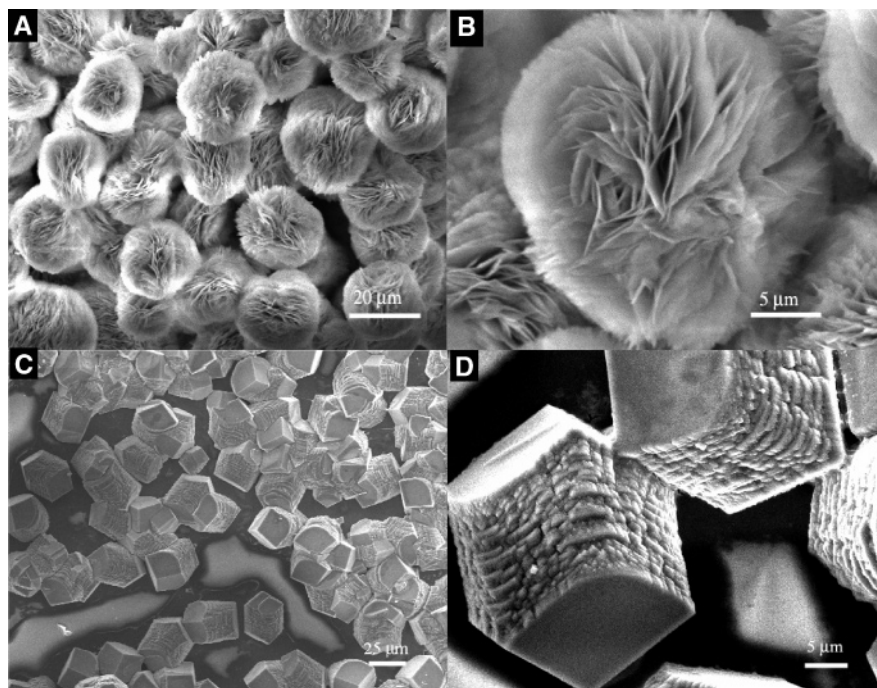


Figure 5. SEM images of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$: (A and B) $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres composed of nanosheets in the presence of 15 mL EG; (C and D) novel hexagonal $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ particle with nanostep structures.

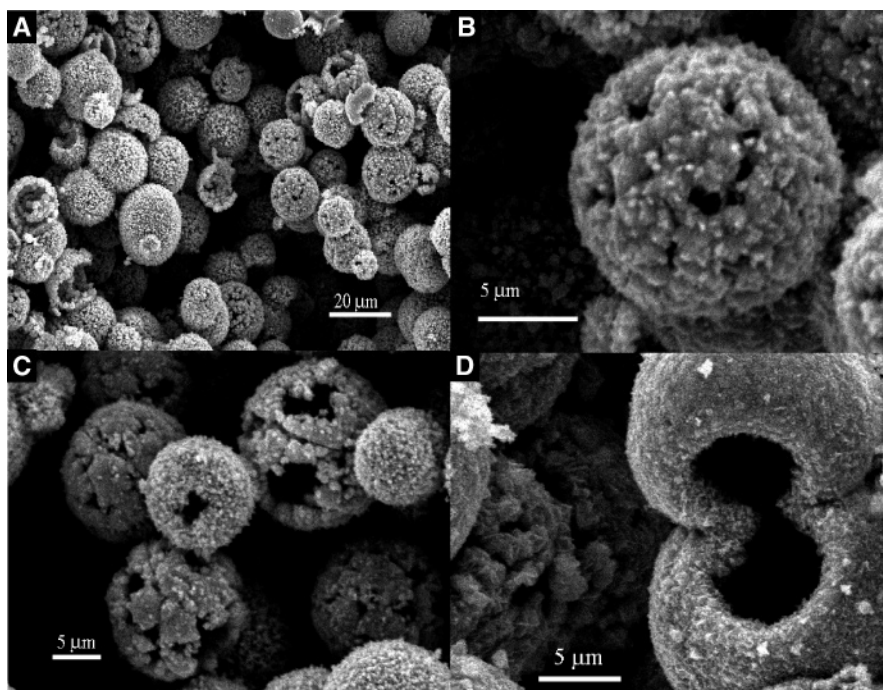
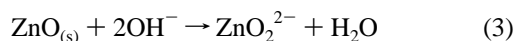
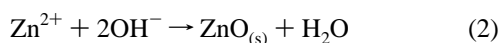
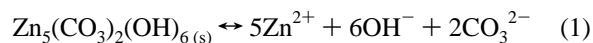


Figure 6. SEM images of the as-synthesized hollow ZnO microsphere by the room-temperature treatment of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres in the KOH solution: (A) Overall product morphology; (B) and (C) detailed view on the surface of hollow ZnO microspheres; (D) twin hollow ZnO microspheres.

excessive, ZnO can be dissolved. The involved chemical reactions may be formulated as:



The reaction occurs simply between $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and KOH in the aqueous solution at room temperature. The increase

of OH^- anion concentration makes reaction 1 move toward the right. Under the strong alkaline conditions, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ can be easily transformed into ZnO due to the fact that the solubility product constant K_{sp} for the $\text{Zn}(\text{OH})_2$ is lower than that of the ZnCO_3 . Therefore, $\text{Zn}(\text{OH})_2$ can be easily obtained at a higher concentration of OH^- , because it forms favorably in comparison with ZnCO_3 . The formation mechanism of ZnO is similar to the case of $\text{Mg}(\text{OH})_2$ proposed by our previous work.²⁰

In the case of the growth of hollow ZnO microspheres, the $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres may be served as sacrificial templates on which the shell grows while the core is consumed

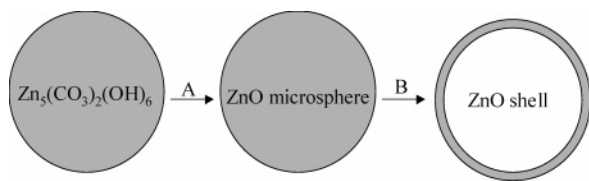


Figure 7. Schematic illustration of the formation of hollow ZnO microspheres: (A) ZnO microspheres prepared by the KOH treatment of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres; (B) ZnO shells prepared by the subsequent KOH treatment of ZnO microspheres.

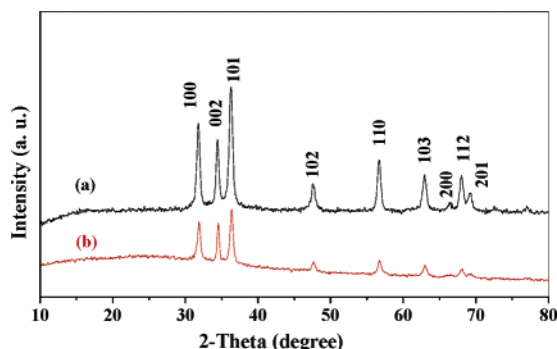


Figure 8. XRD patterns of ZnO samples synthesized by $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ at different temperatures: (a) 450 °C and (b) room temperature.

uniformly. The whole growth mechanism of hollow ZnO microspheres is schematically displayed in Figure 7, which is in agreement with that of hollow calcite spheres reported by Yu et al.²¹ At the early stage of the growth of ZnO shells, monodispersed $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres can be converted to ZnO microspheres by an aging reaction of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and KOH in solution at room temperature. Subsequently, these ZnO microspheres grow at the expense of the dissolving ZnO particles so that the microsphere core acts as a sacrifice template for the growth of ZnO, which has resulted in the hollow ZnO shells (Figure 6). To succeed in converting $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres to hollow ZnO shells, an appropriate amount of OH^- is crucial to the formation of ZnO shells. The lower OH^- concentration can lead to the dissolution of the ZnO core incompletely, whereas when the amount of OH^- is excessive, no ZnO particles can be obtained because ZnO can be completely dissolved.

Besides the above method for the conversion of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ to ZnO under the strong alkaline solution at room temperature, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres can also be converted into ZnO microspheres by a thermal decomposition process. The sphere-like morphology (Figure S6) is well preserved after the heat treatment at 450 °C, and no hollow structure can be obtained. XRD patterns of the obtained ZnO samples are shown in Figure 8, in which two as-prepared ZnO samples (ZnO filled microspheres and hollow microspheres) possess the similar XRD pattern. All strong peaks can be indexed as the pure hexagonal phase of wurtzite-type ZnO (space group: $P6_3mc$) with lattice constants $a = 3.249 \text{ \AA}$ and $c = 5.206 \text{ \AA}$, which agree well with the reported data (JCPDS no. 79-0206). From XRD patterns we can see that the relative intensity of each peak of the ZnO microspheres by calcination at 450 °C (Figure 8a) is stronger than that of the ZnO hollow microspheres (Figure 8b) obtained via a solution-based method at room temperature, which indicates that ZnO synthesized at high-temperature possess a better crystallinity.

4. Conclusion

We have demonstrated the preparation of hydrozincite microspheres with tunable surface architectures via a solvothermal method. The surface architectures of these microspheres, such as nanocubes, nanorods, and nanosheets, can be effectively tuned by concisely controlling the reaction time and the amount of EG. The capping reagent of EG exerts a major influence on directing the formation of these unique microstructures. The hollow ZnO microspheres with a porous surface have been successfully fabricated via a solution-based method by the room-temperature treatment of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres composed of nanocubes. A possible growth mechanism of hollow ZnO microspheres from filled $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres is proposed. The similar shape of filled ZnO microspheres can also be obtained by the direct pyrolysis of filled $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres composed of nanocubes at 450 °C. In contrast to the direct calcination of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ at high temperature, the solution-based method shows a strong ability to control ZnO morphology.

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Supporting Information Available: SEM images of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and ZnO, crystal structure of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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