

ARTICLES

Room Temperature Fabrication of Hollow ZnS and ZnO Architectures by a Sacrificial Template Route

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Hollow ZnS and ZnO architectures are fabricated by employing $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres as the sacrificial template. $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres can be effectively converted into the core/shell structured ZnO/ZnS composites (in the Na_2S solution) and hollow ZnO architectures (in the KOH solution), by a spontaneous ion replacement reaction at room temperature. Removing the core by the KOH treatment of core/shell structured ZnO/ZnS, hollow ZnS spheres with different shell thicknesses can be effectively achieved. The obtained hollow ZnO architectures exhibit unique geometrical shapes, and their walls are composed of nanocrystals, which are connected to each other to form their hemispherical or circular shape. A possible formation process from $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres to core/shell structured ZnO/ZnS composites is proposed by arresting a series of intermediate morphologies.

1. Introduction

One of the important goals of material scientists has been tailoring the structure to obtain particular morphologies for the design and development of new materials for more and more advanced applications.^{1–3} Especially, hollow structures show a lower density, higher surface area, and distinct optical property, which have resulted in various applications in drug delivery,⁴ medical diagnostics,⁵ plasmonics,⁶ and catalysis.⁷ Recently, considerable research efforts have been made to prepare semiconductor materials (e.g., ZnS and ZnO) with a hollow structure, for example, hollow ZnS spheres have been synthesized by using silica⁸ and polystyrene⁹ spheres as the sacrificial template. The double direct templating strategy was also proposed for the synthesis of hollow ZnS microspheres perforated with a periodic array of uniform pores.¹⁰ On the other hand, hollow ZnO spheres have been synthesized by ethanol droplets as soft templates¹¹ or by employing the vapor deposition method.¹² However, until now, it still remains a great challenge to develop facile and environmentally benign methods for creating hollow spherical structures of semiconductor materials.

As a very important direct wide-band-gap semiconductor with the highest $E_g = 3.6$ eV among all II–VI compounds, ZnS has received much attention due to its excellent properties and is extensively used as displays, sensors, and lasers.¹³ As an important wide-band-gap semiconductor with $E_g = 3.37$ eV, ZnO has been of great research interest as a result of its unique applications in catalysts, sensors, piezoelectric transducers and actuators, and photovoltaic and surface acoustic wave devices.¹⁴ For these applications, the morphology control of ZnS and ZnO structures are critical to tune their chemical and physical

properties to the appropriate ones. From the industrial viewpoint, the room temperature fabrication of hollow ZnS and ZnO structures is extremely practical and economic. However, to the best of our knowledge, there are few reports on the room temperature fabrication of hollow ZnS and ZnO architectures.

Inspired by a promising study on the formation of hollow nanocrystals with a controllable void size, wall porosity, and shell thickness through a galvanic replacement reaction between Ag templates and HAuCl_4 with the expense of reactive electrical current in an aqueous medium,¹⁵ we here extend this strategy to the room temperature fabrication of ZnS and ZnO hollow structures via a spontaneous replacement reaction between $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ templates and Na_2S or KOH solution, respectively. $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres can be converted into core/shell structured ZnO/ZnS composites in the Na_2S solution; on the other hand, such microspheres can also be converted into hollow ZnO architectures in the KOH solution. When the core is removed by the KOH treatment of core/shell structured ZnO/ZnS composites, hollow ZnS spherical shells can be effectively achieved. The evolution process from $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ spheres to core/shell structured ZnO/ZnS composites is further investigated. This facile synthetic approach allows us to reduce the growth temperature to room temperature, leading to the development of an effective, low-cost fabrication process that has good potentials for scale-up.

2. Experimental Section

The preparation of hollow ZnS spherical shells involved an initial synthesis of core/shell structured ZnO/ZnS composites and a subsequent removal of cores by the KOH treatment of these composites. In a typical synthesis, 0.065 g of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ powders in a spherical shape (see Supporting Information)

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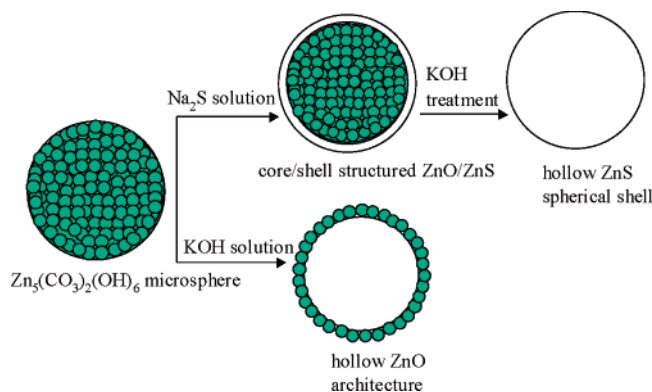


Figure 1. Schematic representation of the microscopic formation of hollow ZnS and ZnO architectures.

were added into 40 mL of deionized water containing 2.4 g of Na_2S powders, under stirring at room temperature (to ensure a good dispersion of these powders in the solution). The mixture solution was kept at room temperature around 2–24 h. The obtained core/shell structured ZnO/ZnS composites were collected, washed with deionized water and absolute ethanol, and dried in air at 60 °C for 4 h. When the cores were removed by the KOH treatment of core/shell structured ZnO/ZnS composites, hollow ZnS spheres with different shell thicknesses were obtained. For hollow ZnO architectures, a typical experiment is 0.0065 g of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ powders in a spherical shape and 0.56 g of KOH were added into 40 mL of distilled water in a beaker. Such a reaction solution was kept for 2–24 h at room temperature. Finally, hollow ZnO architectures were collected, washed several times with distilled water and absolute ethanol, and dried in a vacuum at 60 °C for 4 h. A schematic diagram for the fabrication of both ZnS and ZnO hollow structures is shown in Figure 1. 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. Scanning electron microscopy (SEM) images were taken with a JEOL-5600LV scanning electron microscopy, using an accelerating voltage of 20 kV. Energy-dispersive X-ray (EDX) microanalysis of the samples was performed during SEM measurements.

3. Results and Discussion

The crystal structure of core/shell structured ZnO/ZnS composites is investigated by XRD measurements. A typical XRD pattern is shown in Figure 2a, in which the diffraction peaks corresponding to both ZnO and ZnS can be clearly seen. From Figure 2a, we can deduce that the as-synthesized core/shell structured composites are composed of crystalline ZnS and ZnO. When the ZnO/ZnS composites are treated in the KOH solution, the characteristic peaks of ZnO disappear, as displayed in Figure 2b. All diffraction peaks can be indexed to a typical zinc blende structured ZnS with the cell constant $a = 5.406 \text{ \AA}$, which is consistent with the standard value for bulk ZnS (JCPDS Card No. 05-0566). It can be found that these hollow ZnS spherical shells are crystallites with a cubic zinc blende structure. No diffraction peaks from other crystalline forms are detected, which indicates a high purity and crystallinity of these hollow ZnS samples.

Figure 3 shows the representative SEM images of core/shell structured ZnO/ZnS composites formed by the ion replacement reaction between $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres and Na_2S in solution at room temperature. It can be observed (see Figure

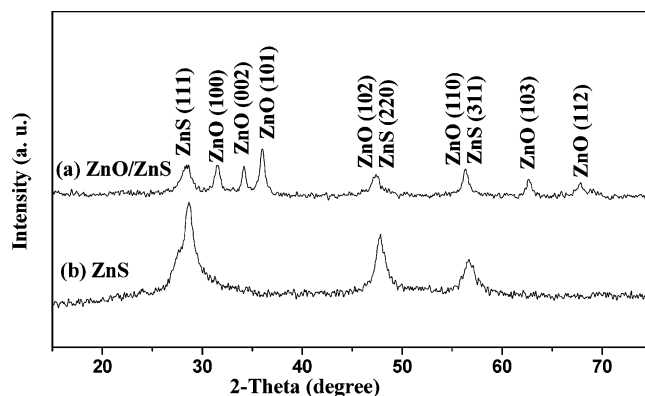


Figure 2. XRD patterns of ZnO/ZnS composites and hollow ZnS spherical shells. (a) Core/shell structured ZnO/ZnS composites by the ion replacement reaction of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres and Na_2S in solution, at room temperature. (b) Hollow ZnS spherical shells prepared by the KOH treatment of core/shell structured ZnO/ZnS composites.

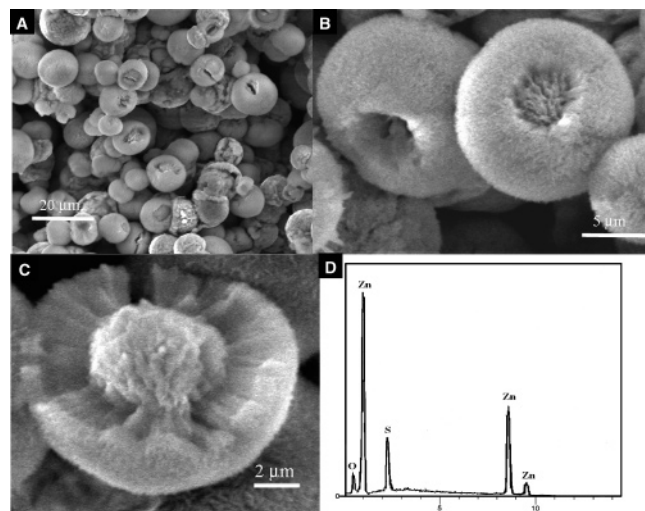


Figure 3. SEM images of core/shell structured ZnO/ZnS composites by the ion replacement reaction of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres and Na_2S in solution, at room temperature. (A) Overall product morphology. (B) Typical broken core/shell structures. (C) A core/shell structure with the broken core and shell. (D) EDX spectrum from the surface of core/shell structures.

3A) that the core/shell structures are already formed after the reaction in 12 h, while the samples retain their spherical morphology well. Figure 3B is the high-magnification SEM image of broken microspheres, which shows that these microspheres have an obvious core/shell structure (in which the inner core can be clearly seen). A careful observation of a typical core/shell structure with a broken shell is shown in Figure 3C, in which the inner core morphology can be observed. It is clearly seen from Figure 3C that the inner core is composed of many tightly aggregated nanoparticles, while the core/shell structured ZnO/ZnS spheres have an average size of 10 μm . EDX analysis is used to determine the local chemical composition of our samples. A typical EDX spectrum is shown in Figure 3D, which exhibits the presence of Zn, O, and S elements. Together with the XRD data, all these results indicate that the core/shell structure is composed of both ZnO and ZnS.

The growth process of core/shell structured ZnO/ZnS composites by employing $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres as the sacrificial template is proposed by arresting a series of inter-

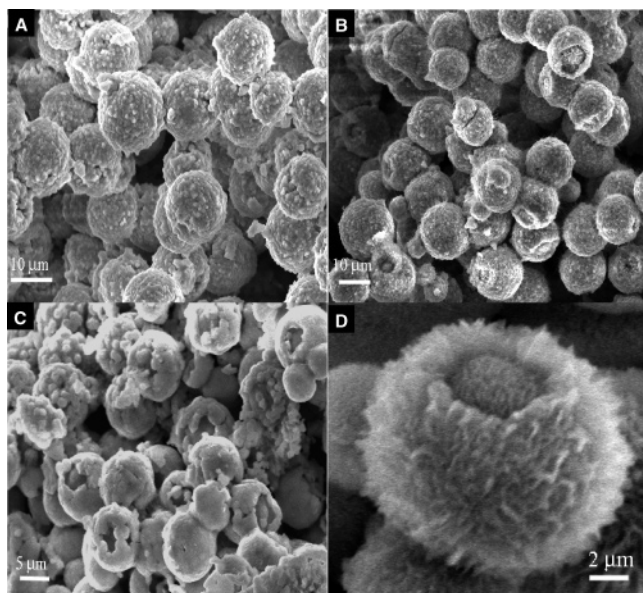


Figure 4. SEM images of particles obtained at different reaction time, showing the evolution of particles from $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres to core/shell structured ZnO/ZnS composites. (A) 0 h ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres). (B) 2 h. (C) 6 h. (D) 16 h.

mediate morphologies. The growth process is monitored by a time-dependent observation. SEM images in Figure 4 show the evolution of particles from $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres to core/shell structured ZnO/ZnS composites. Figure 4A shows the SEM image of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres, which are used as the sacrificial template for the synthesis of core/shell structured ZnO/ZnS composites and hollow ZnO architectures. Figure 4B shows the SEM image of particles produced by the ion replacement reaction between $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ templates and Na_2S solution for around 2 h. It is clearly observed that some core/shell structures begin to form and the surface morphology is well retained (similar to that of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres). When the reaction time reaches 6 h, the SEM observation reveals that a number of spherical shells are gradually separated from their inner cores (Figure 4C), while the surface becomes smooth. With increasing the reaction time up to 12 h, many core/shell structures can be observed (as shown in Figure 3A–C). From Figure 3C it can be clearly seen that the obtained ZnO/ZnS sphere has a core consisting of interconnected and irregularly shaped primary particles. In some cases, the continuous extension of reaction time results in the roughening of the shell surface, while the typical core/shell structures can always be obtained and clearly identified, as displayed in Figure 4D. It may be concluded that the evolution mechanism of particles from $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres to core/shell structured ZnO/ZnS composites is mainly through a dissolution–recrystallization process.

To obtain core/shell structured ZnO/ZnS, we currently select the reaction between $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres and Na_2S solution at room temperature. The conversion from $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres to core/shell structured ZnO/ZnS composites is attributed to the difference of the solubility product for ZnCO_3 (1.2×10^{-10}), ZnO (6.8×10^{-17}), and ZnS (1.2×10^{-24}) at the same temperature.¹⁶ Compared with ZnCO_3 , ZnO and ZnS are more thermodynamically stable due to their lower solubility products. When an appropriate amount of Na_2S is introduced into the reaction solution, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres dissociate slowly to produce Zn^{2+} , OH^- , and CO_3^{2-} ions in solution. The conversion from $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres to core/shell structured ZnO/ZnS composites can be

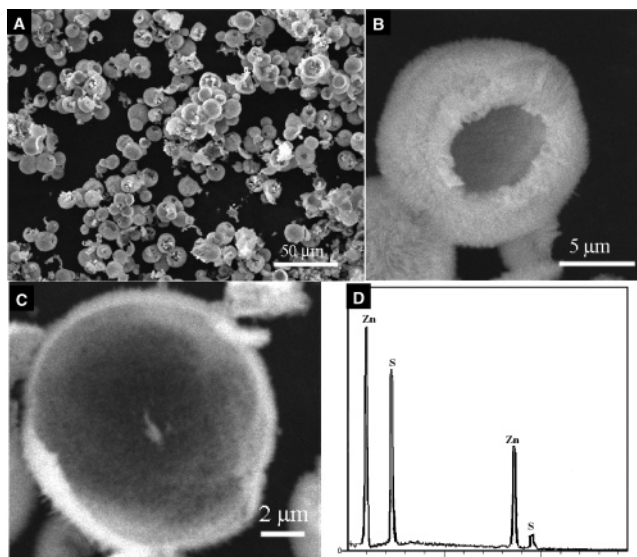
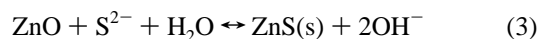
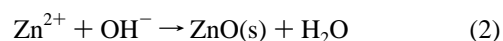
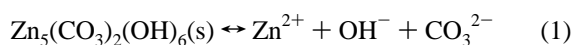


Figure 5. SEM images of hollow ZnS spherical shells after removing their cores through the KOH treatment of ZnO/ZnS core/shell structures. (A) Low-magnification SEM image of ZnS. (B and C) High-magnification SEM images of the ZnS shells with different shell thicknesses. (D) EDX spectrum of the as-synthesized ZnS shell, showing the chemical composition of ZnS shells.

realized by including S^{2-} ions. The involved chemical reactions may be formulated as follows:



For the growth of core/shell structured ZnO/ZnS composites, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres serve as a sacrificial template in the whole process. Two main processes are believed to occur: one is the formation of cores and the other is the formation of shells. A possible mechanism for the formation of ZnO/ZnS core/shell structures can be deduced from the solubility difference. When $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres are introduced into the Na_2S solution, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres can be in situ converted into ZnO microspheres in the alkaline solution, where the solubility difference is the driving force (reaction 2). On the other hand, since S^{2-} ions are uniformly distributed in the whole solution, the surface of ZnO spheres can be transformed into ZnS due to the fact that the solubility product of $[\text{Zn}][\text{S}]$ is smaller than that of $[\text{Zn}][\text{O}]$ (reaction 3). Na_2S solution can act as both alkali source (to convert $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ into ZnO) and sulfur source (to produce ZnS shells). Therefore, ZnO/ZnS core/shell structures can be successfully obtained. If thioacetamide is used instead of Na_2S as the sulfur source at 110 °C, while all other reaction conditions are unchanged, the formation of ZnS particles can be obtained instead of ZnO/ZnS composites. Thioacetamide can react with water at certain temperature to produce H_2S ; ZnS particles are thus formed as a result of the reaction between $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and H_2S in solution. These observations indicate that core/shell structured ZnO/ZnS composites can only be obtained in alkali conditions and in the presence of S^{2-} ions in our present system.

The obtained core/shell structured ZnO/ZnS composites are further treated by the KOH solution, resulting in the pure ZnS shells. Figure 5A shows the SEM image of hollow ZnS products that are obtained by the KOH solution treatment of core/shell

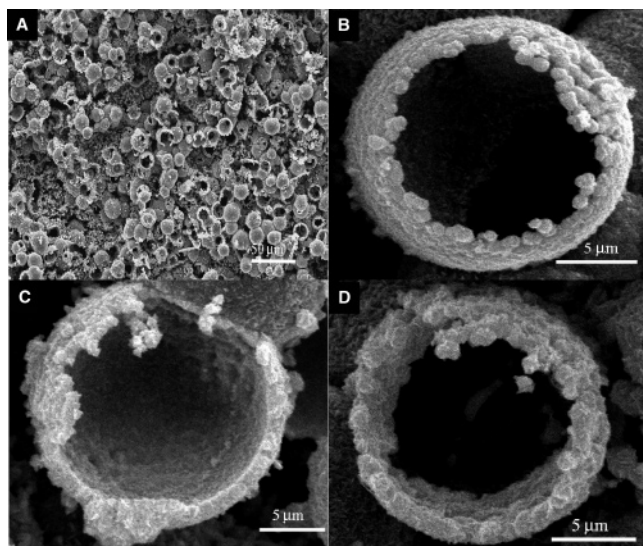


Figure 6. SEM images of hollow ZnO architectures by employing $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres as the sacrificial template. (A) Overall product morphology. (B) Hollow ZnO architecture composed of nanocrystals. (C) Hemispherical ZnO architecture. (D) Circular shaped ZnO architecture.

structured ZnO/ZnS composites; many shell structures can be seen in this process. A closer examination of these samples indicates that they are a hollow structure as presented in the higher magnification image of Figure 5B and C, where a different thickness of ZnS shells is clearly observed. EDX spectrum taken from one typical shell is further used to confirm such a pure composition, as displayed in Figure 5D. This spectrum shows strong peaks of only Zn and S elements, which indicates that all cores have been removed completely. It is evident that the KOH treatment can substantially remove the cores from ZnO/ZnS core/shell structures, which thus results in the formation of ZnS shells. When core/shell structured ZnO/ZnS composites are introduced into the KOH solution, ZnO core can be dissolved by the KOH solution leaving behind ZnS shells. On the basis of the above experimental facts and XRD (Figure 2) and EDX (Figure 3D) analysis, we may draw the conclusion that core/shell structured ZnO/ZnS composites are composed of the ZnS shell and ZnO core.

For a comparative purpose, only KOH is used instead of Na_2S , while all other conditions are well kept. Figure 6 shows SEM images of hollow ZnO architectures via the ion replacement reaction of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres in the KOH solution at room temperature. SEM observation (see Figure 6A) reveals that hollow spheres are formed, while many of them have an open mouth (Figure 6B). An enlarged SEM image from the surface of hemispherical ZnO architectures clearly reveals that the shell of ZnO hollow structures is composed of numerous nanocrystals, as displayed in Figure 6C. In our samples, ZnO microrings can also be identified, as shown in Figure 6D. The wall of microrings consists of many nanocrystals, which are connected each other to form a circularly shaped ring. A possible formation mechanism of hollow ZnO architectures can be described as follows. At first, ZnO spheres can be in situ formed via a reaction between $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ sphere templates and KOH solution, which can be understood in eqs 1 and 2. It should be noted that ZnO spheres can be dissolved by KOH solution since ZnO has an amphoteric character. Subsequently, these ZnO spheres grow at the expense of the dissolving ZnO particles by Ostwald ripening,¹⁷ so that the sphere core acts as a sacrifice template for the growth of outer ZnO layer, resulting in hollow ZnO architectures. The obtained XRD spectrum shown in Figure

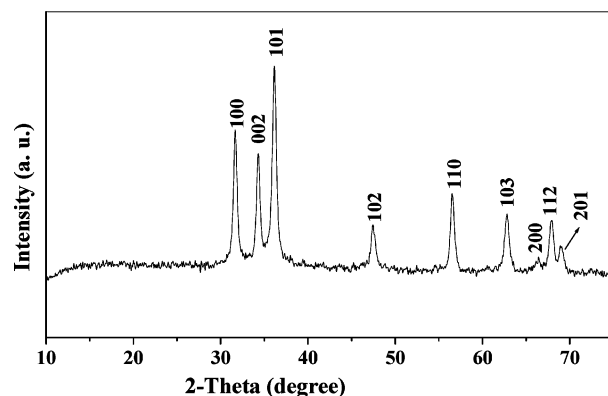


Figure 7. XRD pattern of hollow ZnO architectures obtained by employing $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres as the sacrificial template.

7 confirms the wurtzite structure of hollow ZnO architectures. Only peaks corresponding to the hexagonal ZnO can be observed, with no evidence of other ZnO phases. All strong peaks can be indexed to the pure hexagonal phase ZnO, which agree well with the reported data (JCPDS no. 79-0206).

4. Conclusion

A sacrificial template route to hollow ZnS spherical shells and ZnO architectures via the spontaneous replacement reaction at room temperature has been established in the current work. $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres can be effectively converted into ZnO/ZnS core/shell composites in the Na_2S solution; the subsequent dissolution of cores (in the KOH solution) leads to the formation of hollow ZnS spheres with different shell thicknesses. Hollow ZnO architectures can also be obtained by employing $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres as the sacrifice template in the KOH solution. The wall of hollow ZnO structures is composed of many nanocrystals, which are connected each other to form hollow ZnO architectures with the hemispherical or circular shape. The possible formation process from $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres to core/shell structured ZnO/ZnS composites is proposed by arresting a series of intermediate morphologies at different reaction times. Our experimental results show that hollow ZnS spherical shells and ZnO architectures can be effectively fabricated by employing $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ microspheres as the sacrificial template.

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

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