10402 *J. Phys. Chem. C* **2008,** *112,* 10402–10406

A General Chemical Conversion Route To Synthesize Various ZnO-Based Core/Shell Structures

Y. F. Zhu, D. H. Fan, and W. Z. Shen*

Laboratory of Condensed Matter Spectroscopy and Opto-Electronic Physics, Department of Physics,
Shanghai Jiao Tong University, 1954 Hua Shan Road, Shanghai 200030, People's Republic of China

Received: March 24, 2008; Revised Manuscript Received: April 29, 2008

Core/shell structures often exhibit improved physical and chemical properties. Developing a relatively general, facile, and low temperature synthetic approach for semiconductor core/shell structures with complex compositions is still a particularly challenging work. Here we report a general chemical conversion route to prepare high quality ZnO-based core/shell (ZnO/ZnS, ZnO/Ag_2S, and ZnO/CuS) microspheres using inexpensive and commercially available reagents. The key to the success of our strategy lies in the use of reactive templates to realize the synthesis of various ZnO-based core/shell structures. The yielded core/shell nanostructures were confirmed by transmission electron microscopy, energy-dispersive X-ray analysis, and X-ray diffraction measurements. Photoluminescence of the ZnO/ZnS core/shell microspheres exhibits a distinct enhancement compared with that of the uncoated ZnO microspheres, showing potential application in optoelectronic devices such as ultraviolet light-emitting diodes and diode lasers. The present chemical conversion approach is expected to be employed in a broad range of applications to fabricate innovative semiconductor core/shell structures with different compositions and shapes for unique properties.

1. Introduction

Recently, core/shell structured materials, together with their hollow structures, have attracted much attention in physics, chemistry, and material science communities because of their specific structures and unique properties.[1–7] The core/shell structured materials usually show improved physical and chemical properties for electronics, magnetism, optics, catalysis, mechanics, and electrochemistry.[1–5] The hollow structures are expected to have potential applications in catalysts, sensors, photonic crystals, artificial cells, nanoscale chemical reactors, energy-storage media, and drug-delivery carriers because of the special hollow geometrical shapes and high surface areas.[6,7] A variety of core/shell structures, including noble-metal, hydroxide, semiconductor, and organic material, have been successfully synthesized.[8–15] Among the various above-mentioned core/shell structures, the study of semiconductor materials coated by a thin layer of another semiconductor is of particular interest for the potential applications of such materials in the fields of optics, electronics, and optoelectronics.[11–15]

As an important wide band gap (3.37 eV) semiconductor, zinc oxide (ZnO) has been extensively investigated because of its outstanding optical and electronic properties. To further broaden its application, many works have recently been devoted to the study of ZnO-based core/shell structures. Up to now, several ZnO-based core/shell-type nanostructures, including ZnO/CdS, ZnO/ZnS, ZnO/SnO_2, and ZnO/ZnSe, were explored.[15–19] In spite of these successes, there still exist some challenges for materials scientists to overcome. First, most of the previous reports are concentrated only on the above-mentioned compositions. Some other ZnO-based core/shell structures with distinctive properties and potential application in solar cells, such as ZnO/Ag_2S and ZnO/CuS core/shell structures, have not yet been reported. Second, it is well-known that properties (optical, electrical, chemical, mechanical, etc.) of nanoscale materials are a function of their composition, size, and structural order.[1] However, most of the previously reported synthetic methods are usually suitable for a certain specific semiconductor material.[15–18] In order to realize the extensive study of the physical and chemical properties of core/shell structures and extend their applications, it is desirable to develop a widely applicable strategy to fabricate core/shell structures composed of various compositions. Third, the traditional preparation method usually faces disadvantages related to requiring special equipment and/or high temperatures, which results in a high-cost and energy-consuming synthesis process.[15–18] Therefore, development of a relatively general and low-cost synthetic method is of great importance and quite necessary.

In this article, we have developed a general, facile, and economic way to prepare ZnO-based core/shell microspheres. The key point of the method is to employ the concept of chemical conversion on spherical templates for forming various semiconductor core/shell structures. Compared with the previous reports, the great success of the work reported in this paper is that a general, facile, and economic method has been demonstrated to prepare core/shell structures and two kinds of new ZnO based core/shell structures (ZnO/Ag_2S, and ZnO/CuS) are successfully synthesized. The study on the photoluminescence (PL) spectra of ZnO and ZnO/ZnS core/shell structures at room temperature indicate that the PL property can be highly improved by coating ZnO microspheres with a thin layer of ZnS. We have further expected that the present chemical conversion approach can be used in a broad range of applications to fabricate innovative semiconductor core/shell structures with various compositions and shapes for unique properties.

2. Experimental Details

Synthesis of ZnO Microspheres. Two different solutions, A and B, were used to synthesize spherical structures with different sizes. Solution A was prepared from aqueous solution

---

* Corresponding author. Fax: +86-21-54747552. E-mail wzshen@sjtu.edu.cn

10.1021/jp802545e CCC: $40.75 © 2008 American Chemical Society
Published on Web 06/21/2008

containing 5 mM $Zn(NO_3)_2 \cdot 6H_2O$, 5 mM $C_6H_{12}N_4$, and 1.36 mM $C_6H_5Na_3O_7 \cdot 2H_2O$. Solution B was prepared using the same reactant but with higher concentration, i.e., 25 mM $Zn(NO_3)_2 \cdot 6H_2O$, 25 mM $C_6H_{12}N_4$, and 6.8 mM $C_6H_5Na_3O_7 \cdot 2H_2O$. After the clear solutions were removed into Pyrex glass bottles (the total volume of the reaction mixture was 40 mL), silicon or glass slide substrates were put into the solutions. The sealed bottles were then heated at 90 °C for about 50 min in a conventional laboratory oven. The final products on the silicon or glass slide substrates were washed with deionized water repeatedly to remove any residual chemical salts and dried under air atmosphere. To prepare pure ZnO microspheres, the obtained products were annealed at 400 °C under an air atmosphere for 120 min before they were used for the next step reaction.

Synthesis of ZnO/ZnS Core/Shell Structured Microspheres. The silicon or glass slide substrates with ZnO microspheres on them were transferred into a Pyrex glass bottle containing 0.2 M thioacetamide (TAA). After being sealed, the bottle was heated at 90 °C for 7 h. The final products on the substrates were washed repeatedly and then dried at 60 °C before being used for the next step reaction and further characterization.

Synthesis of ZnO/Ag_2S and ZnO/CuS Core/Shell Structured Microspheres. The metal cation exchange process of ZnS to Ag_2S and CuS was initiated by transferring the as-prepared ZnO/ZnS core/shell structured microspheres into a 50 mM aqueous silver nitrate solution and a mixture solution of 100 mM copper nitrate and 10 mM tartaric acid, respectively. During the reaction process, the solution temperature was kept at 90 °C. For better crystal quality, the as-prepared ZnO/CuS core/shell structured microspheres were annealed at 200 °C for 60 min under argon atmosphere.

Characterization of the Samples. The morphology and structure of the samples were characterized using a field-emission scanning electron microscope (FE-SEM; Philips XL30FEG) with an accelerating voltage of 5 kV and a high-resolution transmission electron microscope (HRTEM; JEOL JEM-2100F). The selected area electron diffraction (SAED) and energy-dispersive X-ray (EDX) microanalysis were also performed during the transmission electron microscope (TEM) measurements. X-ray diffraction (XRD) was carried out on a diffractometer (Bruker/D8 Discover with GADDS) equipped with a Cu K_α source ($\lambda = 1.5406$ Å). PL spectra were recorded at room temperature by a Jobin Yvon LabRAM HR 800UV micro-Raman system under a He−Cd (325.0 nm) laser excitation.

3. Results and Discussion

Structural and Compositional Characterization of ZnO Microspheres. It has been a great challenge to synthesize ZnO microspheres at low temperatures. The major difficulty is that the spherical ZnO structure is not easily yielded because of different growth rates at different crystal directions.[20] Here, we use a strategy similar to that reported in our previous work for producing spherical structures, where a high concentration of trisodium citrate has been employed to control the nucleation and growth rate of ZnO crystal.[21] According to the previous observation, synthesis of $Zn(OH)_2$/ZnO core/shell microspheres can be achieved during this process. In order to fabricate pure ZnO microspheres, we have annealed the as-prepared samples at 400 °C under an air atmosphere for 120 min. Figures 1a and 1b present the FE-SEM images of the prepared ZnO microspheres with different sizes. The sizes of the microspheres could be controlled by changing the concentration of precursor solution during the fabrication process.

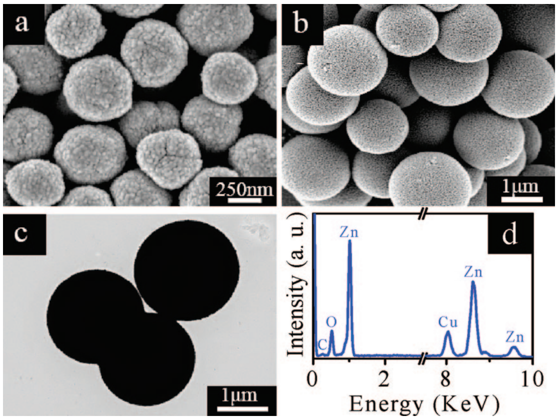

Figure 1. (a and b) FE-SEM images of the ZnO microspheres with different sizes. (c) TEM image of the ZnO microspheres shown in Figure 1b. (d) EDX spectrum of the ZnO microspheres.

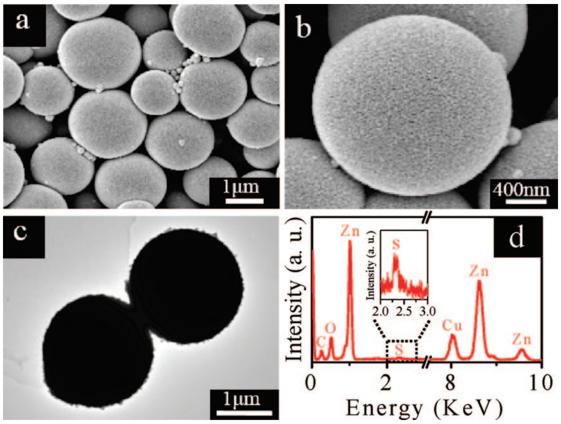

Figure 2. (a) Low- and (b) high-magnification FE-SEM images of the ZnO/ZnS core/shell structured microspheres. (c) TEM image of the ZnO/ZnS core/shell microspheres. (d) EDX spectrum of the corresponding sample with an enlarged sulfur element shown in the inset.

TEM measurements have also been carried out for further investigation of the ZnO microsphere structures. Figure 1c shows the TEM result corresponding to the SEM image of Figure 1b, demonstrating that the prepared ZnO microspheres are solid. The EDX spectrum, shown in Figure 1d, indicates that the obtained microspheres are composed of Zn and O elements. The signal of Cu originates from the copper grid, while the C peak comes from carbon film on the Cu grid. This controllable synthesis of ZnO microspheres provides the possibility of preparing ZnO-based core/shell structures with different sizes, and in the following we will employ the ZnO microspheres with large sizes (as shown in Figure 1b) to realize various ZnO-based core/shell structures as well as ZnS hollow microspheres.

Structural and Compositional Characterization of ZnO/ZnS Core/Shell and ZnS Hollow Microspheres. The main attempt in the present work is to synthesize ZnO/ZnS core/shell structures for the further realization of ZnS hollow and other ZnO-based core/shell microspheres. To make the conversion of ZnO microspheres to ZnO/ZnS core/shell microspheres, we transfer the obtained ZnO microspheres into a solution containing 0.2 M TAA. The TAA solution provides sulfide ions to react with zinc ions dissolved from the ZnO microspheres for forming ZnS. During the reaction process, the solution temperature was kept constant at 90 °C. Figures 2a−c display the FE-SEM and TEM images of the ZnO/ZnS core/shell structured microspheres. Although no significant changes were observed

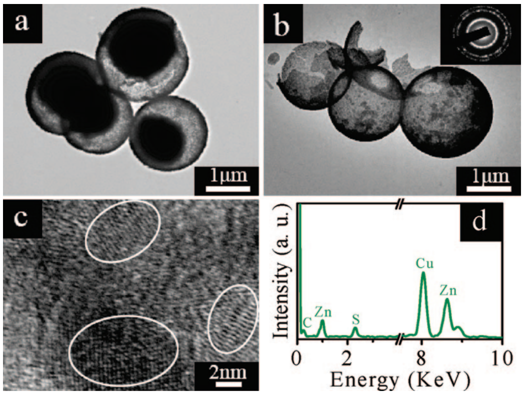

Figure 3. (a) TEM image of the ZnO/ZnS core/shell microspheres treated in a dilute sulfide acid solution for 30 min. (b) TEM image of the ZnS hollow microspheres with the selected area electron diffraction pattern shown in the inset. (c) HRTEM image of a ZnS hollow microsphere shell. (d) EDX spectrum of ZnS hollow microspheres.

in comparison with the morphology of the prepared ZnO microspheres in Figures 1b and 1c, the compositional information of the EDX spectrum in Figure 2d exhibits the presence of Zn, O, and S elements, providing powerful evidence for the successful incorporation of S element into the ZnO microspheres. However, since there is no morphological difference before and after the S incorporation, further evidence is necessary to demonstrate that the prepared microspheres are composed of ZnO cores and ZnS shells.

We have performed an effective experiment to clearly identify the core and shell structures by transferring the as-prepared ZnO/ZnS microspheres into a bottle containing a dilute sulfuric acid solution. This dilute acid solution can react with ZnO to gradually dissolve it without destroying ZnS. Figure 3a shows the TEM image of the sample treated in this acid solution for 30 min at room temperature, from which we can observe that there are hollow interior spaces between the cores and the shells, likely due to the partial dissolution of cores in the acid solution. When the reaction time was increased to 90 min, all of the cores in the microspheres had been removed, as demonstrated in Figure 3b. There is a strong contrast difference in all of the microspheres with a light inner center and relative dark edge, confirming that the obtained microspheres are hollow. The corresponding ring-like SAED pattern (inset in Figure 3b) recorded on a hollow microsphere reveals that the hollow microspheres are of cubic structure and polycrystalline in nature. The diffraction rings from inside to outside can be indexed to (111), (220), and (311) crystal planes of the cubic ZnS, respectively.

HRTEM observation can give further insight into the structural features of these hollow microspheres. The result shown in Figure 3c clearly exhibits that the hollow microsphere shell is mainly composed of ZnS nanocrystalline grains, indicating the polycrystalline nature of the ZnS shell as well. Meanwhile, EDX measurements (Figure 3d) can provide the compositional information of these hollow microspheres. In addition to Cu and C elements, only Zn and S appear in the EDX spectrum without O element, unambiguously confirming that the hollow microspheres in Figure 3b are composed of pure ZnS. Therefore, it is clear that this method can effectively remove the ZnO cores in a short time without destroying the ZnS shells.

XRD characterization can also demonstrate the crystal structure and transformation process of these microspheres. The curves a, b, and c in Figure 4 represent the diffraction patterns of ZnO (shown in Figure 1b), ZnO/ZnS (Figure 2b), and ZnS (Figure 3b) microspheres, respectively. From the curve a, it can be clearly observed that only the peaks corresponding to the hexagonal ZnO structure [powder diffraction file (PDF) No. 36-1451] are detected, confirming that the microspheres before reacting with TAA solution are consist of pure polycrystalline ZnO. The diffraction peaks of cubic ZnS (PDF No. 05-0566) appear after the ZnO microspheres treated in the TAA solution (curve b), indicating the formation of a thin layer of ZnS on the ZnO microspheres. After removal of ZnO in dilute sulfuric acid solution, only the diffraction peaks corresponding to cubic ZnS structure remianed (curve c), suggesting that the microsphere shells are composed of ZnS. On the basis of the above experimental observation and discussion, it can be concluded that the sulfidation process begins at the surface of the ZnO microspheres, resulting in the formation of ZnO (core)/ZnS (shell) structured microspheres.

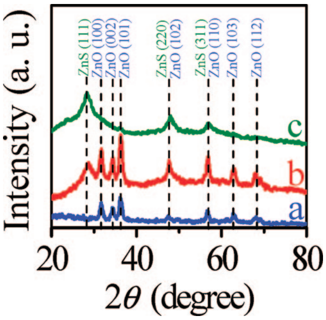

Figure 4. XRD patterns of (a) ZnO microspheres, (b) ZnO/ZnS core/shell microspheres, and (c) ZnS hollow microspheres.

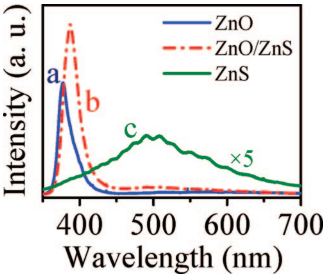

Figure 5. Room-temperature PL spectra of (a) ZnO microspheres, (b) ZnO/ZnS core/shell microspheres, and (c) ZnS hollow microspheres.

PL Properties of ZnO Microspheres and ZnO/ZnS Core/Shell Structures. PL study is a powerful tool to investigate the optical properties of these novel semiconductor structures. We have performed the room-temperature PL to show the improved optical properties of the prepared ZnO/ZnS core/shell microspheres over their individual components (ZnO and ZnS). Figure 5 presents the room-temperature luminescence spectra of ZnO microspheres, ZnO/ZnS core/shell structured microspheres, and ZnS hollow microspheres. The PL spectrum of ZnO microspheres (curve a) shows a strong ultraviolet (UV) emission peak at 377 nm and a negligible green band. It is reported that the UV emission originates from the recombination of free excitons in the near-band-edge of the wide band gap ZnO and the broad visible luminescence has commonly been attributed to the oxygen vacancies of ZnO.[22,23] Therefore, the strong UV peak and negligible green band in curve a indicates the high optical quality of the prepared ZnO microspheres. The high optical quality of the yielded samples can be explained by the fact that the ZnO microspheres are obtained by annealing the $Zn(OH)_2/ZnO$ core/shell microspheres at 400 °C under an air atmosphere, where the density of the defects of oxygen vacancies is very low.[21]

The ZnO/ZnS core/shell microspheres basically exhibit the PL behavior of the ZnO cores with a small redshift (about 10 nm) in the UV region and a distinct enhancement in luminescence intensity (curve b). The redshift in the PL spectrum can be attributed to the strain caused by the lattice mismatch between ZnO and ZnS. Theoretical work has already predicted that the strain in the ZnO/ZnS interface is strong enough to reduce the total system band gap.[24] In addition, a wider band gap semiconductor material (ZnS) coated on the ZnO passivates the surface electronic states of the ZnO cores, resulting in an obvious enhancement in the PL intensity of UV emission. Such an enhancement in the emission has also been observed in the coaxial CdS/ZnS nanowires.[12] To exhibit an improved PL property of the ZnO/ZnS core/shell structures over their single-component counterparts, we have further given the room-temperature PL spectrum of ZnS hollow microspheres (curve c). The PL spectrum only shows a broad weak peak with the center at about 489 nm, similar to the reported results in the PL study of other ZnS nanostructures.[25,26] The periodic ripples are due to the interferometer effect from the filter in the experimental system.

As we know, the previously reported ZnO nanostructures usually contain a large number of oxygen vacancies resulting in a weak UV emission and a strong broad green emission. Compared with the ZnO nanostructures synthesized by conventional processing approaches,[27–29] the ZnO microspheres obtained through the present method possess high optical quality, showing a strong UV emission together with a negligible green band emission. After a thin layer of ZnS was coated on ZnO microspheres, the intensity of UV emission was obviously enhanced. Therefore, these ZnO/ZnS core/shell microspheres are more applicable for the fabrication of optoelectronic devices, such as UV light-emitting diodes and diode lasers.

Advantages of the Present Method. It is worth noting that the present method not only establishes a facile way for synthesizing ZnO/ZnS core/shell structures but also provides a valid approach to prepare ZnS hollow microspheres. The ZnS hollow microspheres have recently attracted considerable interest because of their unique geometrical shapes and wide applications in the fields of energy-storage media, drug-delivery carriers, displays, sensors, and lasers.[30–33] So far, the template synthesis method has commonly been used to synthesize ZnS hollow microspheres, in which the inert spherical structures (polystyrene microspheres, latex particles, SiO_2 colloids, etc.) were employed as templates.[30–33] In these inert-template-directed methods, the introduction of surface functional groups on the templates is often necessary for the effective adsorption of the target precursors.[34] As compared with the conventional template approach, ZnO microspheres serve not only as the templates in the present synthetic procedure but also as the reactant for the subsequent ZnS hollow microsphere formation. As a result, there is no need to perform any additional surface modification, leading to a simple preparation method and a significant reduction in fabrication time.

Figure 6 illustrates the scheme of the whole synthetic process for the above semiconductor core/shell microspheres. A high concentration of trisodium citrate was used to control the nucleation and growth rate of ZnO crystals to form ZnO solid microspheres after annealing (Figure 6a). By using the obtained ZnO microspheres to react with TAA aqueous solution, we could achieve the ZnO/ZnS core/shell structures (Figure 6b). The ZnS hollow microspheres can be further synthesized after treating the prepared ZnO/ZnS core/shell microspheres in dilute sulfide acid solution for about 90 min (Figure 6c). The present chemical conversion method suggests that spherical or other suitably shaped objects composed of reactive material can act as both reactants and templates to synthesize core/shell structures, i.e., we can extend this chemical approach to the synthesis of other ZnO-based core/shell microspheres. Furthermore, all of those reactions mainly take place in an aqueous system, and the synthetic routes are relatively simple, environment-friendly, and therefore suitable for large-scale applications. Figure 6 also schematically shows the formation of ZnO/Ag_2S (Figure 6d) and ZnO/CuS (Figure 6e) core/shell microspheres by transferring the prepared ZnO/ZnS core/shell structured microsphere templates into aqueous solutions containing Ag^+ and Cu^{2+}, respectively.

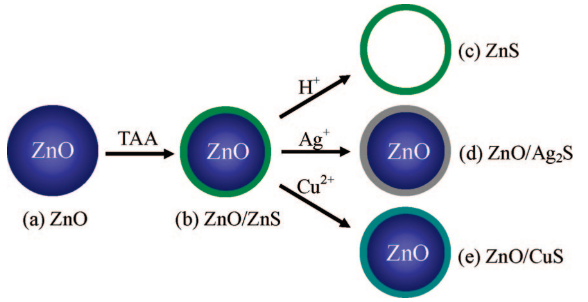

Figure 6. Schematic illustration for the formation processes of ZnO-based core/shell microspheres and ZnS hollow microspheres: (a) ZnO microspheres, (b) ZnO/ZnS core/shell microspheres, (c) ZnS hollow microspheres, (d) ZnO/Ag_2S core/shell microspheres, and (e) ZnO/CuS core/shell microspheres.

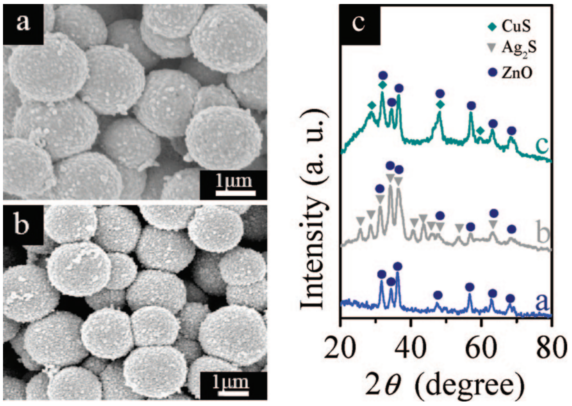

Figure 7. FE-SEM images of (a) ZnO/Ag_2S and (b) ZnO/CuS core/shell microspheres. (c) XRD patterns of (a) ZnO microspheres, (b) ZnO/Ag_2S core/shell microspheres, and (c) ZnO/CuS core/shell microspheres.

Structural Characterization of ZnO/Ag_2S and ZnO/CuS Core/Shell Microspheres. We have successfully synthesized the ZnO/Ag_2S and ZnO/CuS core/shell microspheres along with the above proposal (Figures 6d and 6e). Figures 7a and 7b show the FE-SEM images of the as-prepared ZnO/Ag_2S and ZnO/CuS microspheres. We note that the morphology of the starting material (Figure 2a) is preserved during the reaction process. The driving force for the cation exchange is provided by the large difference in solubility [solubility product constant (K_{sp}) of ZnS is 2.93×10^{-25}, while K_{sp} of Ag_2S is 6.69×10^{-50} and K_{sp} of CuS is 1.27×10^{-36}].[35] The temperature of the aqueous solutions used in this procedure was also kept at around 90 °C to accelerate the reaction process. We have observed a color change of ZnO/ZnS microspheres right after immersing them into the above-mentioned solutions, indicating the formation of new products. After the chemical reaction was finished, we also performed XRD measurements to identify microstructural modifications. Figure 7c presents the diffraction patterns of the yielded core/shell microspheres, together with that of the pure ZnO microspheres for comparison. From Figure 7c, we can see that in addition to the hexagonal ZnO structure (PDF No. 36−1451), diffraction peaks originating from monoclinic Ag_2S (PDF No. 14−0072) and hexagonal CuS (PDF No. 06−0464) also clearly appear, confirming that the reaction products are ZnO/Ag_2S and ZnO/CuS core/shell microspheres.

Perspective. It is reasonable to assume that more ZnO-based core/shell structures can be realized through transferring the ZnO/ZnS core/shell structured microsphere templates into aqueous solutions containing other metal cations under the condition that those yielded metal sulfides have a lower K_{sp} than that of ZnS. Since core/shell structures usually show improved physical and chemical properties compared with their individual materials, these ZnO-based core/shell structures may find broader application in optoelectronic, photocatalytic, and photovoltaic devices than that of pure ZnO structures.[36,37] Furthermore, we can expect that the concept of chemical conversion can be employed to prepare other semiconductor core/shell structures with various geometrical shapes. For example, FeS has an even larger K_{sp} (1.59×10^{-19}) compared with that of ZnS. Synthesis of various FeS-based core/shell structures (including FeS/ZnS, FeS/Ag_2S, FeS/CuS, etc.) may be possible by using different FeS nanostructures (e.g., nanowires, nanorods, nanospheres, etc.) as templates. Therefore, the present chemical conversion process is a general, facile, and economic way to synthesize semiconductor core/shell structures with various compositions and geometries for novel and unique properties.

4. Conclusions

In summary, a general, facile, and economic method is developed to prepare ZnO-based core/shell spheres with tunable sizes. The dimensions of the products are determined by the size of the starting ZnO spheres (from about 500 to 2000 nm) which can be controlled by changing the concentration of the precursor solution. During the synthesis process, we used a structure-directing agent, trisodium citrate, to control the nucleation and growth rate of crystal for producing spherical structures and then subsequently annealed the products for forming ZnO microspheres. The synthesis of ZnO-based core/shell microspheres (ZnO/ZnS, ZnO/Ag_2S, and ZnO/CuS) as well as pure ZnS hollow microspheres is realized by employing the prepared reactive microspheres as templates through a chemical conversion technique. Although the current work focuses on ZnO-based core/shell microspheres, other semiconductor core/shell structures with various shapes are expected to be synthesized under conditions that reactive templates are used during the chemical conversion process. The present chemical conversion approach opens up possibilities for extensive study of the physical and chemical properties of the yielded semiconductor core/shell structures, broadening their potential applications in electronics, magnetism, optics, catalysis, mechanics, electrochemistry, etc.

Acknowledgment. This work was supported by the Natural Science Foundation of China under contracts 10734020 and 10674094, National Major Basic Research Project of 2006CB921507, National Minister of Education Program of IRT0524, and Shanghai Municipal Key Project of 06JC14039.

References and Notes

(1) (a) Caruso, F. *Adv. Mater.* **2001**, *13*, 11. (b) Yang, Z.; Cong, H.; Cao, W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4284.

(2) (a) Wang, J.; Loh, K. P.; Zhong, Y. L.; Lin, M.; Ding, J.; Foo, Y. L. *Chem. Mater.* **2007**, *19*, 2566. (b) Qian, H. S.; Yu, S. H.; Luo, L. B.; Gong, J. Y.; Fei, L. F.; Liu, X. M. *Chem. Mater.* **2006**, *18*, 2102.

(3) (a) Sun, Y.-K.; Myung, S.-T.; Kim, M.-H.; Prakash, J.; Amine, K. *J. Am. Chem. Soc.* **2005**, *127*, 13411. (b) Fu, L. J.; Liu, H.; Zhang, H. P.; Li, C.; Zhang, T.; Wu, Y. P.; Holze, R.; Wu, H. Q. *Electrochem. Commun.* **2006**, *8*, 1.

(4) Salgueirino-Maceira, V.; Correa-Duarte, M. A.; Spasova, M.; Liz-Marzan, L. M.; Farle, M. *Adv. Funct. Mater.* **2006**, *16*, 509.

(5) Liang, Z.; Susha, A.; Caruso, F. *Chem. Mater.* **2003**, *15*, 3176.

(6) (a) Guo, L.; Liang, F.; Wen, X.; Yang, S.; He, L.; Zheng, W.; Chen, C.; Zhong, Q. *Adv. Funct. Mater.* **2007**, *17*, 425. (b) Han, J.; Song G, P.; Guo, R. *Chem. Mater.* **2007**, *19*, 973. (c) Deng, Z.; Chen, W. M.; Zhou, S. X.; You, B.; Wu, L. M. *Langmuir* **2006**, *22*, 6403.

(7) (a) Dinsmore, A. D.; Hsu, M. F.; Nikolaides, M. G.; Marquez, M.; Bausch, A. R.; Weitz1, D. A. *Science* **2002**, *298*, 1006. (b) Sulieman, K. M.; Huang, X. T.; Liu, J. P.; Tang, M. *Nanotechnology* **2006**, *17*, 4950.

(8) Lee, C. C.; Chen, D. H. *Nanotechnology* **2006**, *17*, 3094.

(9) Lin, Y. S.; Hung, Y.; Lin, H. Y.; Tseng, Y. H.; Chen, Y. F.; Mou, C. Y. *Adv. Mater.* **2007**, *19*, 577.

(10) Jang, J.; Nam, Y.; Yoon, H. *Adv. Mater.* **2005**, *17*, 1382.

(11) Hsu, Y. J.; Lu, S. Y.; Lin, Y. F. *Adv. Funct. Mater.* **2005**, *15*, 1350.

(12) Datta, A.; Panda, S. K.; Chaudhuri, S. *J. Phys. Chem. C* **2007**, *111*, 17260.

(13) (a) Yan, C. L.; Xue, D. F. *J. Phys. Chem. B* **2006**, *110*, 25850. (b) Zhang, H.; Yang, D.; Ma, X.; Que, D. *Nanotechnology* **2005**, *16*, 2721.

(14) Li, J.; Zhao, D.; Meng, X.; Zhang, Z.; Zhang, J.; Shen, D.; Lu, Y.; Fan, X. *J. Phys. Chem. B* **2006**, *110*, 14685.

(15) Wang, X.; Gao, P.; Li, J.; Summers, C. J.; Wang, Z. L. *Adv. Mater.* **2002**, *14*, 1732.

(16) Gao, T.; Li, Q.; Wang, T. *Chem. Mater.* **2005**, *17*, 887.

(17) Wang, W. W.; Zhu, Y. J.; Yang, L. X. *Adv. Funct. Mater.* **2007**, *17*, 59.

(18) Panda, S. K.; Dev, A.; Chaudhuri, S. *J. Phys. Chem. C* **2007**, *111*, 5039.

(19) Geng, J.; Liu, B.; Xu, L.; Hu, F. N.; Zhu, J. J. *Langmuir* **2007**, *23*, 10286.

(20) Umar, A.; Hahn, Y. B. *Appl. Phys. Lett.* **2006**, *88*, 173120.

(21) Zhu, Y. F.; Fan, D. H.; Shen, W. Z. *J. Phys. Chem. C* **2007**, *111*, 18629.

(22) Vanheusden, K.; Warren, W. L.; Seager, C. H.; Tallant, D. K.; Voigt, J. A.; Gnade, B. E. *J. Appl. Phys.* **1996**, *79*, 7983.

(23) Duan, J. X.; Huang, X. T.; Wang, E.; Ai, H. H. *Nanotechnology* **2006**, *17*, 1786.

(24) Schrier, J.; Demchenko, D. O.; Wang, L. W. *Nano Lett.* **2007**, *7*, 2377.

(25) Shen, G.; Bando, Y.; Golberg, D. *Appl. Phys. Lett.* **2006**, *88*, 123107.

(26) Gong, J. F.; Yang, S. G.; Duan, J. H.; Zhang, R.; Du, Y. W. *Chem. Commun.* **2005**, 351.

(27) Fan, D. H.; Shen, W. Z.; Zheng, M. J.; Zhu, Y. F.; Lu, J. J. *J. Phys. Chem. C* **2007**, *111*, 9116.

(28) Shen, G. Z.; Bando, Y.; Lee, C. J. *J. Phys. Chem. B* **2005**, *109*, 10578.

(29) (a) Zhang, Y.; Zhang, W. F.; Zheng, H. W. *Scr. Mater.* **2007**, *57*, 313. (b) Lu, H. B.; Liao, L.; Li, J. C.; Wang, D. F.; He, H.; Fu, Q.; Xu, L.; Tian, Y. *J. Phys. Chem. B* **2006**, *110*, 23211.

(30) Wolosiuk, A.; Armagan, O.; Braun, P. V. *J. Am. Chem. Soc.* **2005**, *127*, 16356.

(31) Hosein, I. D.; Liddell, C. M. *Langmuir* **2007**, *23*, 2892.

(32) Huang, K. J.; Rajendran, P.; Liddell, C. M. *J. Colloid Interface Sci.* **2007**, *308*, 112.

(33) Zhou, H.; Fan, T.; Zhang, D.; Guo, Q.; Ogawa, H. *Chem. Mater.* **2007**, *19*, 2144.

(34) San, H.; Jang, B.; Kim, T.; Oh, S. M.; Hyeon, T. *Adv. Funct. Mater.* **2005**, *15*, 1845.

(35) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 69th ed.; CRC Press: Boca Raton, FL, 1988−1989.

(36) Ding, G. Q.; Shen, W. Z.; Zheng, M. J.; Fan, D. H. *Appl. Phys. Lett.* **2006**, *88*, 103106.

(37) Wei, H.; Wu, Y.; Lun, N.; Hu, C. *Mater. Sci. Eng., A* **2005**, *393*, 80.

JP802545E