Chinese Chemical Letters Vol. 15, No. 6, pp 733-736, 2004
http://www.imm.ac.cn/journal/ccl.html

A Simple Method for the Preparation of ZnO Prickly Spheres

Da Zhi LI, Xin Yu SONG, Si Xiu SUN*, Jin Xin GUO

School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100

Abstract: The synthesis of ZnO prickly spheres using precipitation followed by heating treatment was investigated. $Zn(OH)_2$ precursor was prepared by precipitation process using $Zn(CH_3COO)_2{\cdot}2H_2O$ in mixed 1-propanol-water solvent. Sodium dodecyl sulfate (SDS) as the anionic surfactant was added to control the morphology. The size and structure of ZnO prickly spheres were studied using XRD, TEM and SEM. The results showed that the morphologies and size of the spheres strongly depended on the volume ratio of 1-propanol /water and molar ratio of SDS/Zn^{2+}. ZnO prickly spheres composed of nanorods could be obtained, when the volume ratio of 1-propanol/water = 2:3 and the molar ratio of Zn^{2+}/SDS ≈ 450:1.

Keywords: ZnO, prickly sphere, precipitation-heat treatment, SDS.

In recent years, synthesized ZnO with different morphologies have considerable interest for scientific research due to their importance in mesoscopic physics and their potential applications. ZnO with various morphologies have been prepared such as nanospheres, one-dimensional structure (nanorods, nanowires and nanotubes), fractal shape (flower and prism)[1-5]etc. Many synthetic routes have been used to prepare nano- or microscaled ZnO particles in various sizes and morphologies over the past few years. For example, hydrothermal method, microemulsion route and thermal precipitation [1-4] *etc*.

About ZnO spheres especially prickly spheres, there were a very few reports except that of Zhang Jun[2], in which prickly spheres were obtained by using ethanol as solvent, $[Zn(OH)_4]^{2+}$ as precursor through a solution approach when the pH was 10. However, the surface of the sphere was not smooth; the nanorods, which formed sphere, were not tightly arranged. In this paper, the ZnO micro- prickly spheres composed of nanorods were successfully fabricated. Simultaneously the nanorods were tightly arranged. The simple approach (precipitation—heat treatment) to fabrication of ZnO prickly spheres by dehydration of the precursor obtained via chemical reaction between $Zn(CH_3COO)_2{\cdot}2H_2O$ and $NH_3{\cdot}H_2O$ in the presence of surfactant (SDS) was reported. Compared with other methods the reaction condition was considerably moderate and the temperature was lower. Moreover, prickly spheres could be obtained in high yield.

Experimental

All the reagents were of analytical grade and without further purification before utilization.

* E-mail: ssx@sdu.edu.cn

ZnO prickly spheres were prepared through two steps. (1) precipitation process: At room temperature $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in mixed 1-propanol-water with SDS for preparing Zn^{2+} saturated solution. Then concentrated ammonia was dropped into the solution until the pH was about 7. The mixed system was filtrated and the precursors were washed several times with anhydrous ethanol in order to obtain purer precursors, which was dried in oven for 20 hours at 70℃. The dried precipitates were confirmed to be $Zn(OH)_2$ by XRD. (2) dehydration: The precursors were dehydrated for 2 hours in oven at 200℃. The as-prepared product was identified by X-ray powder diffraction (XRD). The morphologies and dimensions of the products were observed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

Result and Discussion

Figure 1 X-ray diffraction spectra of ZnO prickly spheres

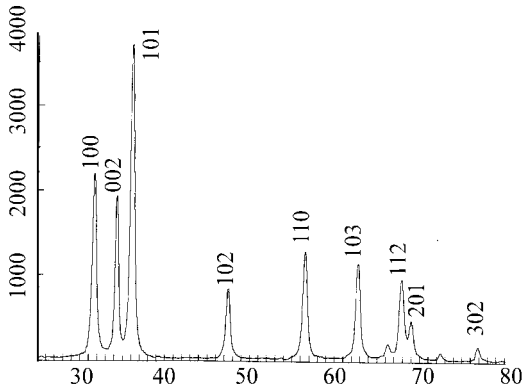
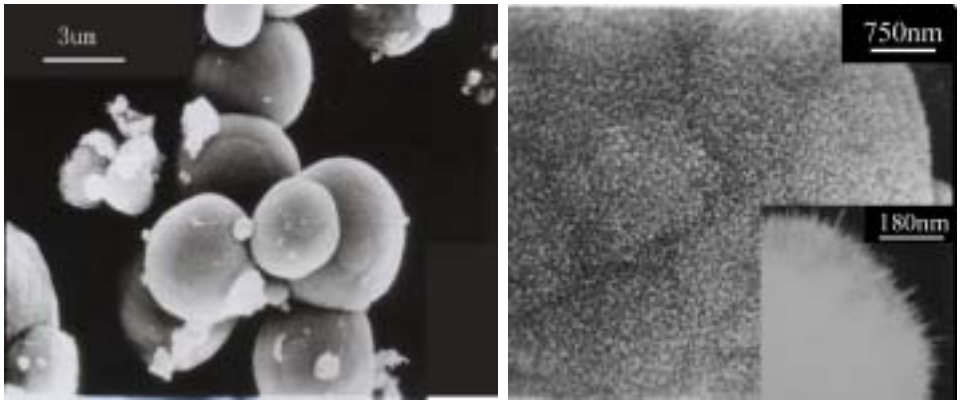


Figure 1 shows the X-ray diffraction spectra of the ZnO prickly spheres. It was obvious that all peaks can be identified as wurtzite structure and no characteristic peaks of impurities. Thus the results showed that the as—prepared product was single phase ZnO.

Figure 2a showed SEM micrographs of ZnO particles obtained when the molar ratio of Zn^{2+}/ SDS ≈ 450:1 and the volume ratio of 1-propanol/ water = 2:3. Spheres with the average diameter 2μm were found. **Figure 2b** was a magnified sphere with relatively smoother surface. The surface of the sphere was so smooth that it was difficult to find the sphere was composed of nanorods. The ZnO prickly sphere consisted of nanorods could be seen clearly from the TEM micrograph (**Figure 2b inset**), though the nanorods were arranged tightly.

To further study on the mechanism for the formation of these spheres, the molar ratio of the Zn^{2+}/SDS was fixed at 450:1, and the volume ratio of 1-propanol/water was changed. The results showed that such prickly spheres could not form. It might be due to the difference polarity between water and 1-propanol. Obviously the volume ratio of 1-propanol/ water was a very important factor for the synthesis of ZnO prickly spheres.

Figure 2 TEM and SEM micrographs of the products.



a b

In the other comparative experiments, it was found that ZnO prickly spheres composed of nanorods could not be obtained when the molar ratio of Zn^{2+}/SDS ≠ 450:1 and the other conditions were fixed. Clearly, SDS played an important role in synthesizing ZnO prickly spheres.

In addition, ZnO prickly spheres had been obtained when 1-propanol was substituted by ethanol at the molar ratio of Zn^{2+}/ SDS ≈ 450:1 and the volume ratio of ethanol/water ＝3:2. We could find 3:2＜2:3 (the volume ratio of 1-propanol/water ＝2:3). The different polarity between ethanol and 1-propanol might be the vital factor. In another way, the average diameter of the spheres was decreased when 1-propanol was substituted by ethanol. We considered: (1) the alcohol might significantly decrease the critical micelle concentration (CMC) of SDS due to their different polarity from water. (2) SDS was thought to be able to act a template. A detailed study for the effect of SDS and alcohol on the process of ZnO prickly spheres is in progress.

Conclusion

In summary, ZnO prickly spheres with average diameter of about 2μm have been successfully prepared by a simple method. The as-prepared ZnO prickly spheres were composed of nanorods. Moreover the usage of SDS and alcoholic environment are two vital factors in synthesizing ZnO prickly spheres. The average diameter of spheres may be controlled by changing different alcohols in mixed solvent.

Acknowledgment

Financial support for this work from National Natural Science Foundation of China (No. 20171029).

References

1. C. Pacholski, A. Kornowski, H. Weller, *J.Angew.Chem.*, *Int.Ed.,* **2002,** *41*, 1188.

2. J. Zhang, L.D. Sun, C.S. Liao, C.H. Yan, *Chin. J. of Inorg. Chem.*, **2002,***18*, 72.
3. H.M. Deng, L. Ding, Y. SHi, X.Y. Liu, J. Wang, *J. Mater. Sci.*, **2001,***36*, 3273.
4. C.K. Xu, G.D. Xu, Y.K. Liu, G.H. Wang, *J. Solid State Commun.*, **2002**, *122*, 175.
5. J.H. Jin, B.X. Bai, T. Bai, X.SH. Xu, *J. Inorg. Chem., Industry*, **2000**,*11*,7.

Received 19 May, 2003