Hydrothermal Synthesis of Zinc Hydroxide Chloride Sheets and Their Conversion to ZnO

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We report a simple hydrothermal slow cooling process to synthesize zinc hydroxide chloride (ZHC) powders consisting of large-sized single-crystal sheets. The lateral size of the sheetlike products can be tuned from 20 to 500 μm through the control of pH condition of the starting zinc chloride solution and the amount of the solute. The growth mechanism of the ZHC sheets is explained by dissolution at high temperatures and precipitation during slow cooling. The ZHC single-crystal sheets were converted to highly oriented polycrystalline zinc oxide sheets by calcination at 500 °C for 5 h in air.

1. Introduction

Metal hydroxide salts (MHS) with layered structures have been widely studied for applications in ion exchange, catalysis, biosensor, and absorption/separation.[1−4] They usually have a general formula of $M_a(OH)_b(X^{c-})_{(2a-b)/c}{\cdot}nH_2O$, where M = Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, etc. They structurally consist of positively charged brucite-like layers of metal hydroxides that require the presence of interlayer anions to maintain overall charge neutrality. These interlayer anions (X) [4−6] can be Cl^-, NO_3^-, CO_3^{2-}, CH_3COO^-, and SO_4^{2-}. The common synthesis methods of the MHS include coprecipitation method[7−9] and hydrothermal method,[10−12] and the obtained products usually have the lamellar morphologies such as films, sheets, and plates.[5,11,13] Among them, the hydrothermal method is more favorable to producing well-crystallized MHS. Current research is mainly focused on producing nanomaterials of MHS such as nanoparticles, nanosheets, nanorods, and nanotubes.[14−18] However, it is also important to develop a synthesis method to produce large crystals of MHS which can present more intrinsic properties and can be used to explore other potential applications. Furthermore, large MHS can also be precursors to obtain tabular metal oxides by thermal decomposition method.[13]

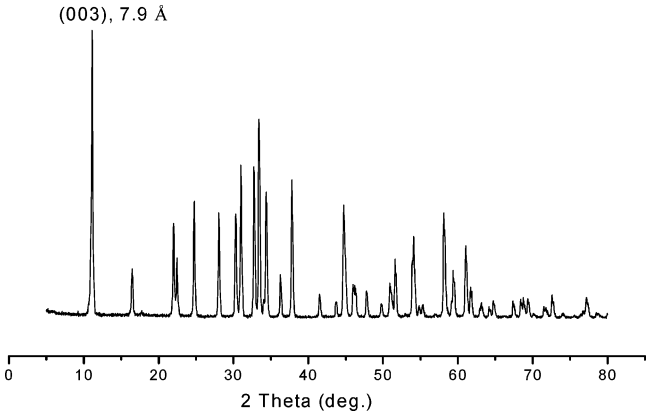

Figure 1. XRD patterns of as-synthesized ZHC sheets from 1 M $ZnCl_2$ solution (pH = 6).

In this paper, we synthesized the zinc hydroxide chloride (ZHC) sheets by a simple hydrothermal method and first reported the ZHC sheets with a very large lateral size beyond 500 μm to the best of our knowledge. After thermal treatments, the ZHC sheets were transformed to sheetlike dense ZnO. Here we select the ZHC for two reasons. First, it is well-known that ZnO usually has *c*-axis oriented growth habits,[19−23] which make the tabular ZnO particles difficult

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(1) Xu, Z. P.; Lu, G. Q. *Pure Appl. Chem.* **2006**, *78* (9), 1771.
(2) Taibi, M.; Ammar, S.; Jouini, N.; Fievet, F.; Molinie, P.; Drillon, M. *J. Mater. Chem.* **2002**, *12* (11), 3238.
(3) Dekany, I.; Berger, F.; Imrik, K.; Lagaly, G. *Colloid Polym. Sci.* **1997**, *275* (7), 681.
(4) Newman, S. P.; Jones, W. *J. Solid State Chem.* **1999**, *148* (1), 26.
(5) Poul, L.; Jouini, N.; Fievet, F. *Chem. Mater.* **2000**, *12* (10), 3123.
(6) Hawthorne, F. C.; Sokolova, E. *Can. Mineral.* **2002**, *40*, 939.
(7) Lea, D.; Malha, B. B.; Richard, P.; Joeel, C.; Philippe, L.; Laurent, C.; Fabrice, L.; Christine, T. G.; Bruno, P. *Nano Lett.* **2006**, *6* (2), 199.
(8) Gursky, J. A.; Blough, S. D.; Luna, C.; Gomez, C.; Luevano, A. N.; Gardner, E. *J. Am. Chem. Soc.* **2006**, *128* (26), 8376.
(9) Vial, S.; Forano, C.; Shan, D.; Mousty, C.; Barhoumi, H.; Martelet, C.; Jaffrezic, N. *Mater. Sci. Eng., C.* **2006**, *26* (2−3), 387.
(10) Miao, J. Y.; Xue, M.; Itoh, H. S.; Feng, Q. *J. Mater. Chem.* **2006**, *16* (5), 474.
(11) Xu, Z. P.; Lu, G. Q. *Chem. Mater.* **2005**, *17* (5), 1055.
(12) Ogawa, M.; Asai, S. *Chem. Mater.* **2000**, *12* (11), 3253.
(13) Morioka, H.; Tagaya, H.; Kadokawa, J. I.; Chiba, K. *J. Mater. Sci. Lett.* **1999**, *18*, 995.
(14) Lee, J. H.; Rhee, S. W.; Jung, D. Y. *Chem. Mater.* **2006**, *18* (20), 4740.
(15) Venugopal, B. R.; Ravishankar, N.; Perrey, C. R.; Shivakumara, C.; Rajamathi, M. *J. Phys. Chem. B* **2006**, *110* (2), 772.
(16) Xu, Z. P.; Stevenson, G. S.; Lu, C. Q.; Lu, G. Q.; Bartlett, P. F.; Gray, P. P. *J. Am. Chem. Soc.* **2006**, *128* (1), 36.
(17) Sun, G.; Sun, L. N.; Wen, H.; Jia, Z. Q.; Huang, K. L.; Hu, C. W. *J. Phys. Chem. B* **2006**, *110* (27), 13375.
(18) Liu, Z. P.; Ma, R. Z.; Osada, M.; Iyi, N.; Ebina, Y.; Takada, K.; Sasaki, T. *J. Am. Chem. Soc.* **2006**, *128* (14), 4872.
(19) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947.
(20) Yan, H. Q.; He, R. R.; Pham, J.; Yang, P. D. *Adv. Mater.* **2003**, *15*, 402.
(21) Huang, L. S.; Wright, S.; Yang, S. G.; Shen, D. Z.; Gu, B. X.; Du, Y. W. *J. Phys. Chem. B* **2004**, *108*, 19901.
(22) Liu, B.; Zeng, H. C. *Langmuir* **2004**, *20*, 4196.

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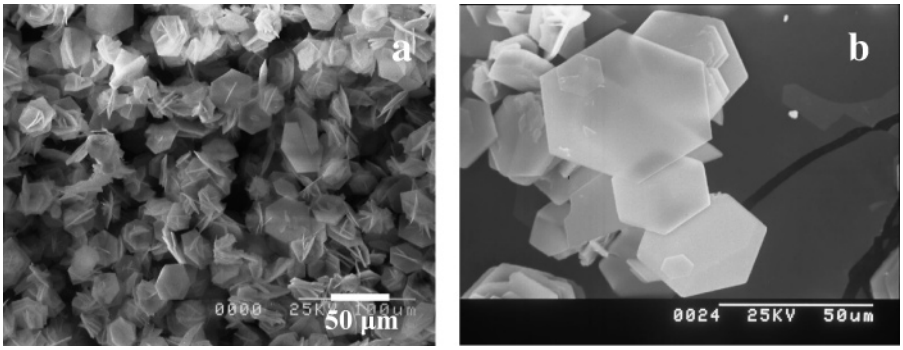


Figure 2. SEM photos of ZHC sheets obtained from 1 M $ZnCl_2$ solution (pH = 6). (a) Overall image; (b) observation with high magnification.

to be obtained.[24−27] It is expected that tabular ZnO materials can be massively synthesized by thermal decomposition of tabular ZHC crystals. Second, the intercalated Cl^- in ZHC is smaller than other anions such as NO_3^-, CO_3^{2-}, CH_3COO^-, and SO_4^{2-}, which is favorable to producing dense structure after thermal decomposition. Morioka et al.[13] reported the production of filmlike ZnO powders by thermal treatment of $Zn_5(OH)_8(COOCH_3)_2 \cdot 2H_2O$. However, the obtained ZnO products were quite porous, which might be ascribed to the release of large anions (CH_3COO^-) from the layers in the original structure.

For hydrothermal synthesis of the metal hydroxide salts, the growth mechanism is supposed to be the traditional dissolution−reprecipitation process and the pH condition is quite important for controlling the phase and morphologies.[11,28,29] As in our former report, ZnO is the preferable phase and ZHC is not obtained in strong basic solutions.[30] Thus, the pH condition in the starting solutions should be carefully controlled to obtain the ZHC phase. Furthermore, the morphologies of MHS are also related to the intercalated anions, starting materials, and reaction temperatures. In this study, the growth conditions were carefully controlled to obtain large ZHC crystals.

2. Experimental Procedure

All reagents are of analytical grade (Wako Pure Chem. Ind.) without further purification. $ZnCl_2$ was dissolved in the distilled water to get 1 M standard solution. Its pH value was around 6 with some white precipitates. NaOH was added to get alkaline solutions (NaOH 0.06−0.4 M) when $ZnCl_2$ solutions were prepared. The starting solution (60 mL) was then transferred into a Teflon-lined autoclave with 75% filling ratio and hydrothermally treated at 220 °C without agitation. After the temperature was maintained at 220 °C for 2 h, the autoclave was cooled down to room temperature at the rate of 1 °C/min. After the reaction, the white powders were harvested and washed by distilled water. The thermal decomposition of the obtained ZHC was conducted to obtain ZnO at 500 °C for 5 h in air. The obtained products were characterized by scanning electron microscopy (SEM, Hitachi S-530), X-ray diffraction (XRD, Rigaku RTP-300 RC) with Cu Kα radiation (40 kV, 100 mA), and transmission electron microscopy (TEM, Hitachi H-800). Thermal analysis (TG/DTA, Seiko TG/DTA 6300 equipped with mass spectrometer) was performed at a constant heating and cooling rate of 5 °C/min in air.

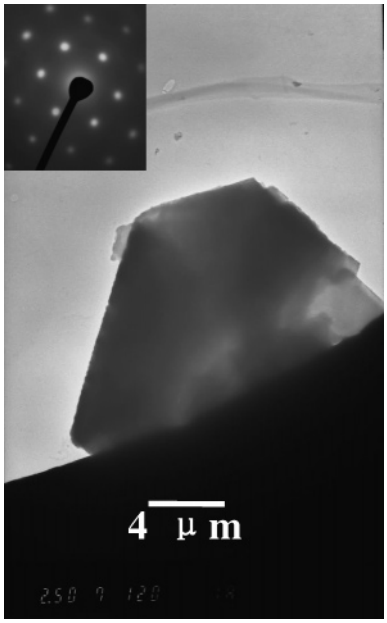


Figure 3. SAED and TEM photo of a ZHC sheet obtained by hydrothermal treatment of 1 M $ZnCl_2$ solutions (pH = 6).

3. Results

3.1. Preparation of ZHC Sheets from the Standard $ZnCl_2$ Solution (1 M, pH = 6). Figure 1 shows the XRD pattern of the product obtained by the hydrothermal slow cooling of 1 M $ZnCl_2$ solution (pH = 6) at the rate of 1 °C/min from 220 °C. The product was confirmed to be $Zn_5(OH)_8Cl_2 \cdot H_2O$ (JCPDS card: 07-0155) and no impurity phases were found. SEM photos (Figure 2) show that the obtained sheets have hexagonal shape. The average tubular size of the ZHC sheets is around 20 μm and the thickness is about 1 μm. TEM observation and SAED show that all the sheets are single crystals (Figure 3). The slow cooling rate (1 °C/min) in our experiments is very important for synthesizing large ZHC sheets. When the autoclave was quickly cooled in air from 220 °C, the obtained product consisted of small and thick plates with rough surface (Figure 4).

(23) Yu, W. D.; Li, X. M.; Gao, X. D. *Cryst. Growth Des.* **2005**, *5*, 151.
(24) Tian, Z. R.; Voigt, J. A.; Liu, J.; Mckenzie, B.; Mcdermott, M. J.; Rodriguez, M. A.; Konishi, H.; Xu, H. F. *Nat. Mater.* **2003**, *2*, 821.
(25) Chen, S. J.; Liu, Y. C.; Shao, C. L.; Mu, R.; Lu, Y. M.; Zhang, J. Y.; Shen, D. Z.; Fan, X. W. *Adv. Mater.* **2005**, *17*, 586.
(26) Illy, B.; Shollock, B. A.; Macmanus-Driscoll, J. L.; Ryan, M. P. *Nanotechnology* **2005**, *16*, 320.
(27) Hu, J. Q.; Bando, Y.; Zhan, J. H.; Li, Y. B.; Sekiguchi, T. *Appl. Phys. Lett.* **2003**, *83*, 4414.
(28) Stanimires, T.; Kirov, G.; Dinolova, E. *J. Mater. Sci. Lett.* **2001**, *20*, 453.
(29) Braterman, P. S.; Xu, Z. P.; Yarberry, F. *Handbook of Layered Materials*; Marcel Dekker: New York, 2004; p 373.
(30) Zhang, W. X.; Yanagisawa, K. *Chem. Lett.* **2005**, *34*, 1170.

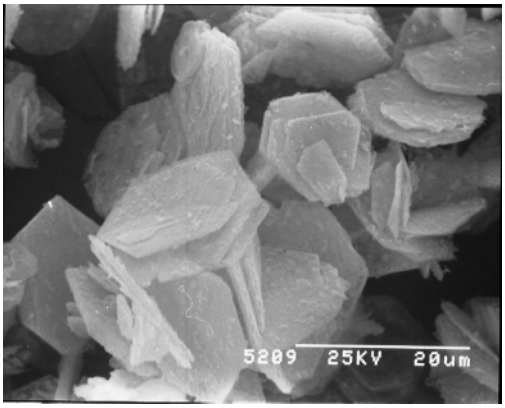
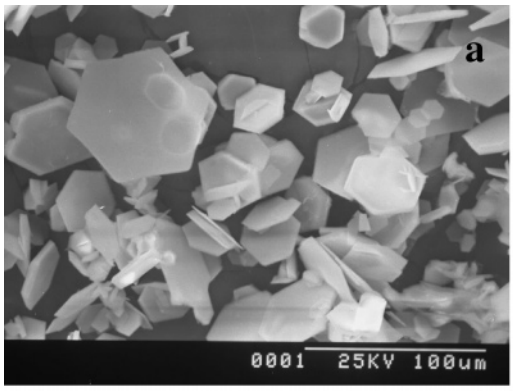


Figure 4. SEM photo of ZHC sheets obtained from 1 M $ZnCl_2$ solution (pH = 6) by quick cooling from 220 °C.



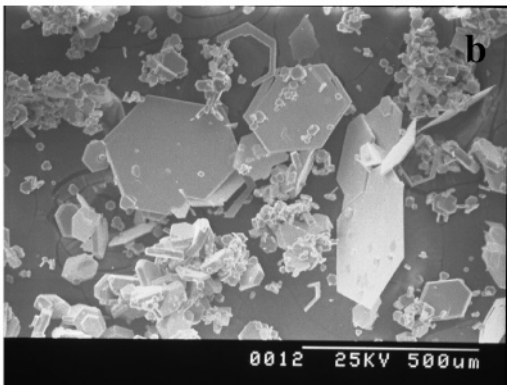
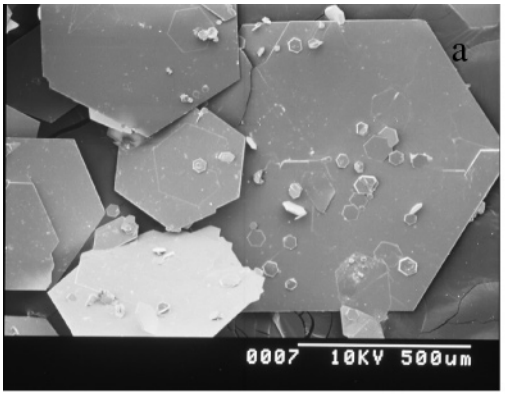
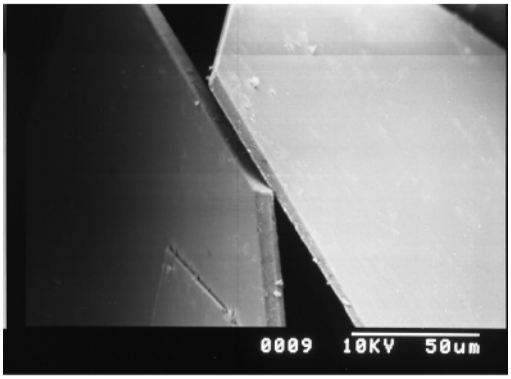


Figure 5. SEM photos of products obtained from 1 M $ZnCl_2$ solutions with different basicity: (a) 0.06 M NaOH; (b) 0.4 M NaOH.

3.2. Effects of NaOH Addition on the Morphology. When the pH value in the starting solutions was increased by addition of NaOH, both the thickness and lateral size of the ZHC sheets increased accordingly. The average lateral size of the ZHC sheets obtained in 1 M $ZnCl_2$ solution (pH = 6) was 20 μm (Figure 2), but the sheets obtained in 0.06 M NaOH solution (pH = 11) increased to around 50 μm (Figure 5a). In 0.4 M NaOH solution, the largest ZHC sheets were 400 μm in lateral size (Figure 5b), but coexisted with small particles in which ZnO phase was found by XRD.

When the $ZnCl_2$ concentration in the starting solution is increased, the acidity accordingly increases and the precipitates gradually disappear. Two molar $ZnCl_2$ solution was a clear solution and no product was collected after hydrothermal reaction. The addition of NaOH to adjust the pH value to 6 resulted in the formation of precipitates in the starting solution and increase in lateral size and thickness of ZHC sheets after the hydrothermal treatment. Thus, the above results indicate that the neutral condition formed in the 1 M standard solution is better for synthesizing pure and thin sheetlike ZHC crystals.





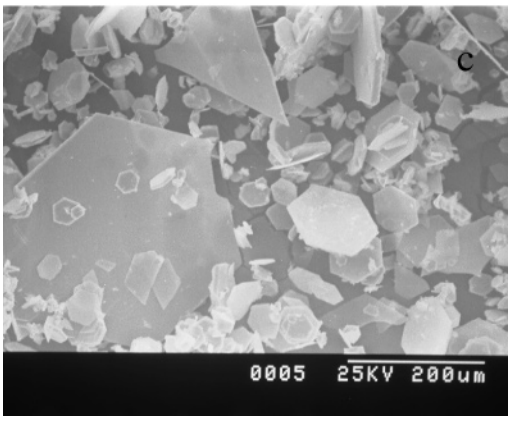


Figure 6. SEM photos of the ZHC crystals obtained from 1 M $ZnCl_2$ solution with addition of ZHC precipitates. (a) and (b) 0.39 g of ZHC precipitates; (c) 0.95 g of ZHC precipitates.

3.3. Effects of the Amount of ZHC Precipitates in the Starting Solution. The weight of ZHC precipitates obtained in 60 mL of 1 M $ZnCl_2$ solution (pH = 6) was about 0.11 g. In our experiments, the amount of precipitates in 1 M $ZnCl_2$ solution (60 mL) is gradually increased by addition of the precipitates collected from other batches. Figures 6a and 6b show the SEM photos of the ZHC sheets obtained with 0.39 g of ZHC precipitates in the starting solutions. It is obviously observed that the obtained ZHC sheets have larger lateral size than those obtained in 1 M $ZnCl_2$ solution with 0.11 g of ZHC precipitates (Figure 2), and the largest lateral size can be more than 500 μm. However, with the increase of ZHC precipitates addition in the starting solutions,

the size inhomogeneity increased, and the product obtained by addition of the precipitates of 0.95 g consisted of smaller particles (Figure 6c). Further addition of the precipitates resulted in serious agglomeration of the small crystals at the bottom of the Teflon liner.

3.4. Conversion of ZHC into Zinc Oxide by Heat Treatment. By calcination, ZHC is converted to zinc oxide by release of HCl and H_2O, as shown in eq 1.

$$Zn_5(OH)_8Cl_2{\cdot}H_2O = 5ZnO + 2HCl\ (13.2\ mass\ \%) + 4H_2O\ (13.1\ mass\ \%) \quad (eq\ 1)$$

TG-DTA investigations were conducted to determine the thermal behavior of the obtained ZHC sheets. The DTA plot presents three endothermic peaks at 180, 202, and 432 °C, respectively, which correspond to three weight loss stages (Figure 7). The thermal mass analysis shows that the first two endothermic peaks at 180 and 202 °C correspond to the release of water. Thus, the loss (13.2%) at higher temperatures (220−432 °C) is attributed to the release of HCl and matches well with the expected theoretical value. The total weight loss up to 500 °C is about 27%, which is comparable with the expected 26.3% in the formula.

After heat treatment of ZHC crystals at 220 °C for 2 h, the XRD result (Figure 8) shows that the sample consists of the low crystalline ZHC phase and the (003) peak shift to higher angle. By heat treatment at 500 °C for 5 h, the ZHC phase is transformed into pure ZnO (Figure 8b). The extremely high intensity of the (002) peak proves the highly *c*-axis oriented structure in ZnO particles. SEM photos show that the obtained ZnO particles completely maintain the sheetlike morphology of ZHC crystals (Figure 9). The cross section (Figure 9b) of a large sheet shows that the obtained ZnO sheets consist of column-like particles arrays and a boundary is observed in the center of the cross section of the thick ZnO sheet.

4. Discussion

4.1. Growth Mechanisms of the ZHC Crystals. When the 1 M $ZnCl_2$ starting solution (pH = 6) was prepared, white precipitates were formed in the solution. The XRD result reveals that these precipitates are pure ZHC phase, and TEM photo shows that they are very thin sheets with hexagonal shape (Figure 10). These precipitates were completely dissolved by heating up to 90 °C and reappeared after cooling down to room temperature. This result suggests that the solubility of ZHC has a positive temperature coefficient. When the white precipitates were removed by centrifugation, no products were obtained after the hydrothermal treatment. Thus, crystal growth by hydrothermal treatment can be explained by the dissolution−reprecipitation process,[30] which has been widely used for flux slow cooling method. First, the ZHC precipitates are completely dissolved in the solution by heating to 220 °C. Then, the nuclei appear by spontaneous nucleation during the cooling stage and grow into large sheetlike precipitates by slow cooling. The fast cooling gave a large number of the nuclei and fast crystal growth, which resulted in the formation of small and thick ZHC plates with rough surface (Figure 4).

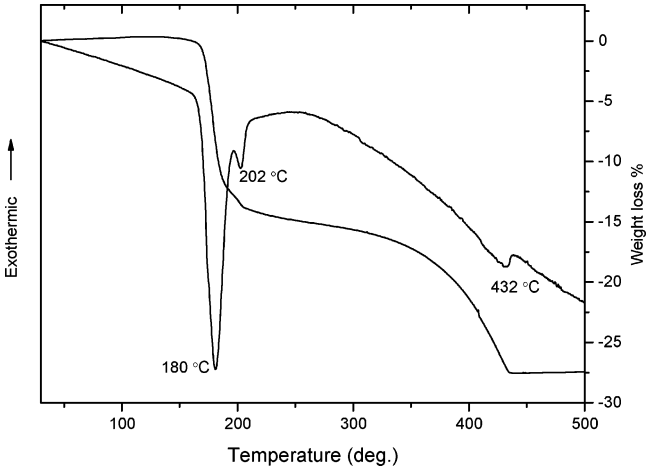


Figure 7. TG-DTA results of the ZHC sheets.

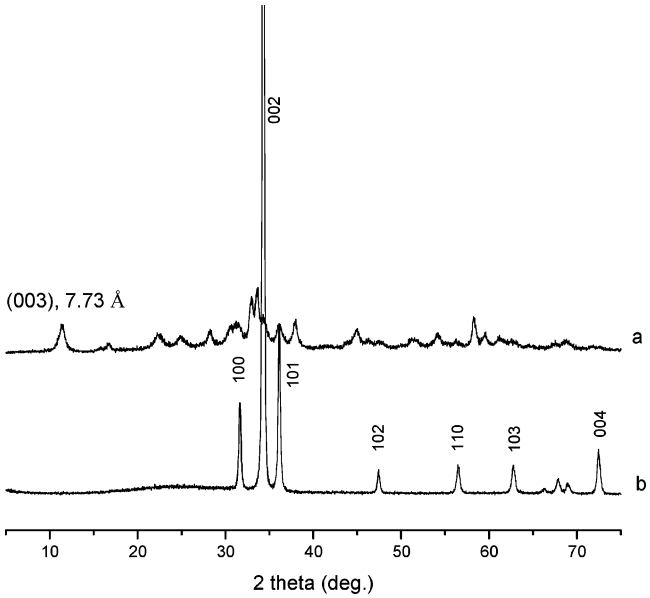


Figure 8. XRD pattern of products obtained by calcination of ZHC crystals at (a) 220 °C for 2 h and (b) 500 °C for 5 h in air.

In the case of 1 M standard $ZnCl_2$ solution, ZHC crystals must start to grow at lower than 90 °C. The increase of ZHC precipitates to 0.39 g in 1 M $ZnCl_2$ solution gave very large ZHC sheets as large as 500 μm (Figure 6a) by slow cooling from 220 °C. It is expected that 0.39 g of ZHC precipitates would be completely dissolved in the solution at 220 °C and the nuclei would be homogenously formed during the slow cooling stage. Thus, by the addition of the precipitates into 1 M $ZnCl_2$ solution, the crystal growth period is increased during the cooling stage and the ZHC sheets grow larger. While in the case of the addition of the precipitate of 0.95 g, the ZHC precipitates might not be completely dissolved in the solution at 220 °C and many undissolved precipitates produce the small crystals, which results in the size inhomogeneity (Figure 6c). The dissolved amount of ZHC in 60 mL of 1 M $ZnCl_2$ solution at 220 °C is estimated to be in the range from 0.39 to 0.95 g by the size homogeneity of ZHC sheets obtained by slow cooling from 220 °C.

The pH conditions must have large effects on the morphology and the phase stability of ZHC because ZHC includes hydroxide ions. The addition of NaOH can increase the amount of the ZHC precipitates in the starting solution

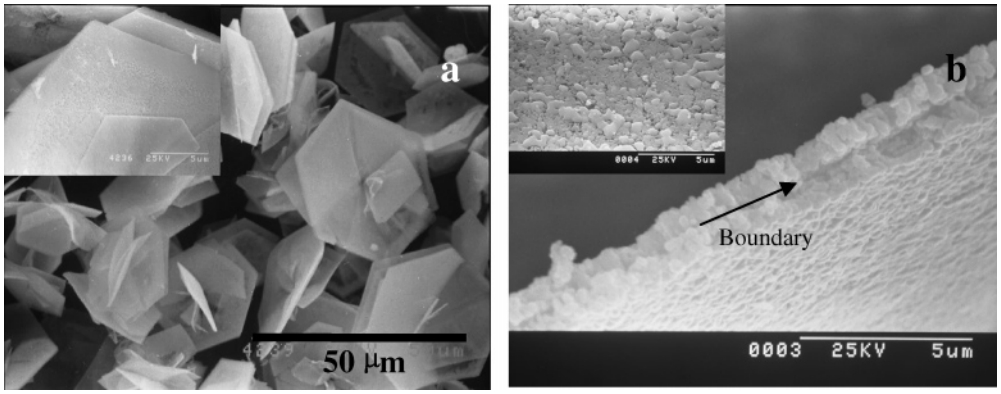


Figure 9. SEM photos of ZnO sheets obtained by calcination of ZHC crystals at 500 °C for 5 h. (a) Small-sized sheets obtained from 1 M $ZnCl_2$ standard solution. (b) Large-sized sheet obtained from 1 M $ZnCl_2$ solution with the addition of 0.39 g of ZHC precipitates. The inset picture is the surface view of the sheet.

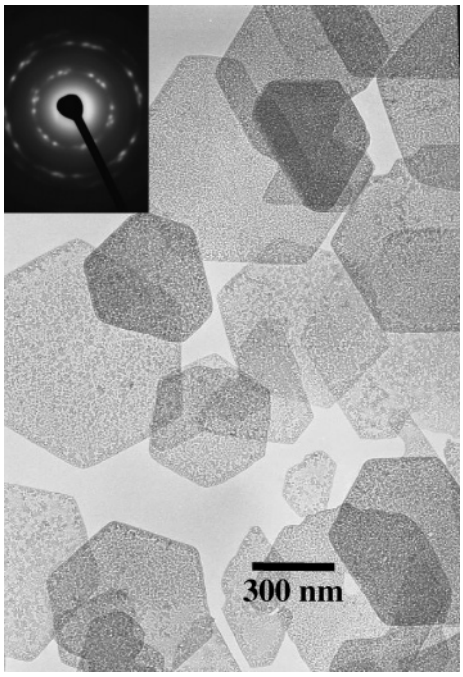


Figure 10. TEM and ED photos of the precipitates in 1 M $ZnCl_2$ starting solution (pH = 6).

and the yield after hydrothermal reaction. In 0.06 M NaOH solution, the product size is increased in both lateral and thickness directions (Figure 5a), but the addition of NaOH up to 0.4 M results in large size inhomogeneity of ZHC sheets (Figure 5b). These results are expected since Zn^{2+} ion is quite sensitive to the pH conditions. It is reported that Zn^{2+} exists in different forms in the solution with different pH condition, that is, $ZnCl_n(OH)_{6-n}$ in acid or neutral condition[31] and $Zn(OH)_4^{2-}$ in basic solution.[32] Accordingly, the growth units are different, which is supposed to affect the growth rate of the crystalline facets. Figure 5 shows that the addition of NaOH obviously increases the growth rate of the *c*-axis direction to give thick sheets. To obtain thin ZHC sheets, the starting solution should be kept around neutral and the lateral size can be increased by increasing the amount of ZHC precipitates in the neutral starting solution.

(31) Harris, D. J.; Brodholt, J. P. *J. Phys. Chem. A* **2003**, *107*, 1050.
(32) Demianets, L. N.; Kostomarov, D. V.; Kuz'mina, I. P.; Pushko, S. V. *Crystallogr. Rep.* **2002**, *47*, S86.

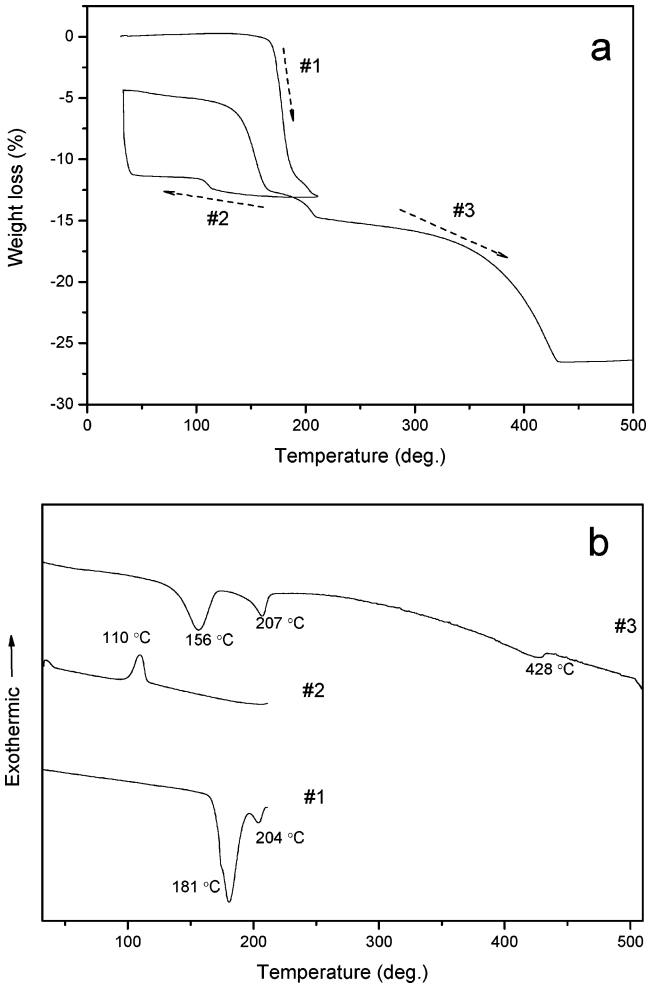


Figure 11. TG (a) and DTA (b) results of the ZHC sheets with reversible process from 30 to 220 °C. (1) Heating from 30 to 220 °C; (2) cooling from 220 to 30 °C and maintaining for 5 h; (3) reheating from 30 to 500 °C.

4.2. Conversion Mechanism of the ZHC Crystals to ZnO Polycrystalline Particles. In the TG-DTA curve (Figure 7), the weight loss at 180 °C is about 9%, which is much larger than the expected 3.3% weight loss of the intercalated water. It indicates that the loss of intercalated water is partially overlapped by the dehydroxylation process. The reversed thermal analysis of the ZHC sample was conducted by heating to 220 °C (Figure 11, line #1), cooling down to room temperature and remaining there for 5 h

(Figure 11, line #2), and finally heating up to 500 °C (Figure 11, line #3). The sample reabsorbs water at 110 °C during cooling down and at room temperature during keeping for 5 h (line #2). The total weight gain is about 7% which is smaller than the weight loss by heating the original sample to 220 °C. This result suggests that the structure of ZHC was partially destroyed by heating to 220 °C. By calcinations at 220 °C for 2 h, the shift of the (003) peak to a higher angle is ascribed to the loss of crystalline water and the broadening of the peaks may be due to the partial collapse of the layered structure (Figure 8a).

The reheating clearly shows the two reversible steps of the dehydroxylation process at 156 and 207 °C (line #3), respectively, in a manner similar to the TG-DTA curve of the original ZHC (Figure 7). In the ZHC structure, Zn has two different positions, Zn(1) in an octahedron and Zn(2) in a tetrahedron.[6] The two steps of the dehydroxylation process are supposed to relate to the two different oxygen positions in hydroxyl which is connected to two different Zn ions.

After calcinations at 500 °C for 5 h, the obtained ZnO sheets (Figure 9) maintain the sheetlike morphology very well and have a denser structure than the reported results by Morioka et al.[13] because of the well-controlled sheet morphology of ZHC crystals and small Cl^- in the ZHS structure. The high (002) orientation in the XRD pattern (Figure 8b) can be ascribed to the oriented alignment of columnlike particles (Figure 9b), which is explained by a surface nucleation procedure. During the heat treatment, the ZnO nuclei first appear on the surface of the ZHC sheets. Then, these nuclei grow inside during the heating and form the columnlike particles, and finally meet with each other in the middle of the sheets to form the boundary (Figure 9b).

5. Conclusions

ZHC sheets were successfully synthesized by hydrothermal slow cooling method from 220 °C at the rate of 1 °C/min. The ZHC sheets synthesized in 1 M $ZnCl_2$ standard solutions (pH = 6) had the average lateral size of 20 μm and the thickness of 1 μm. The addition of a small amount of NaOH in the starting solution increased the sheet size, but the addition of a large amount resulted in the formation of ZnO. On the other hand, with the addition of 0.39 g of ZHC precipitates in the starting solution, the average lateral size of the ZHC sheets was largely increased and the largest lateral size was beyond 500 μm. The growth mechanism can be explained by dissolution−reprecipitation procedure with homogeneous nucleation. It was confirmed on the basis of TG-DTA results that the ZHC phase was converted to ZnO by heat treatment at 432 °C. After calcinations at 500 °C for 5 h in air, ZnO sheets consisting of highly *c*-axis oriented columnlike particles arrays were produced. The ZnO sheets inherited well the morphology from ZHC crystals.

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