

Shape control synthesis of low-dimensional calcium sulfate

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Abstract. Calcium sulfate nanorods, nanowires, nanobelts and sheets had been synthesized via a facile solution reaction of CaCl_2 and H_2SO_4 in mixed solvents of ethanol/*N,N*-dimethylformamide and deionized water at 35°C. The results indicated that well-crystallized CaSO_4 nanomaterials with different morphology were obtained by adjusting the volume ratio of ethanol/*N,N*-dimethylformamide to deionized water and the reaction time. Samples prepared at 35°C in mixed solvents of 50 mL ethanol and 30 mL water for 1 min and 2 h showed nanowire and sheet morphology, respectively. While increasing the volume ratio of ethanol to deionized water to 78/2, only nanorods were obtained. When *N,N*-dimethylformamide was employed to substitute ethanol, the sample heating at 35°C for 2 h was composed of nanowires in 50 mL *N,N*-dimethylformamide and 30 mL water. Higher volume ratio of *N,N*-dimethylformamide to deionized water caused the formation of nanorods.

Keywords. Calcium sulfate; nanomaterials; crystal growth; microstructure.

1. Introduction

Calcium sulfate abundantly exists in nature in three different forms according to the degree of hydration: gypsum (calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), bassanite (calcium sulfate hemihydrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and anhydrite (CaSO_4). Calcium sulfate is a very important industrial material which is used as food additive, paper-making material, timbering, medical material, inorganic filler or intensifier in composite (Winn and Hollinger 2000; McKee *et al* 2002; Nilsson *et al* 2002; Baux *et al* 2008). The size, morphology and structure of crystals have great effects on their properties. Low-dimensional nanostructured materials such as nanotubes, nanorods/nanowires, nanobelts/nanoribbons and nanosheets are receiving more attention (Duan *et al* 2001; Huang *et al* 2001; Huynh *et al* 2002). Up to now, different morphologies of nanosized calcium sulfate, such as nanoparticles (Rees *et al* 1999), nanorods (Chen *et al* 2007), nanowires (or nanofibres) (Rees *et al* 1999; Kuang *et al* 2002; Chen *et al* 2007), nanotubes (Chen *et al* 2007), and nanosheets (Song *et al* 2003) have been prepared. The synthesis of CaSO_4 powders has been carried out mainly through microemulsion/reverse micelle methods and organic-assisted synthesis method, which required not only critical preparation parameters but also complex reaction technique. In this paper, we expect a facile synthesis of CaSO_4 crystals through the adjustment of the solvents using ethanol and *N,N*-dimethylformamide (DMF), in which the product has a smaller solubility compared to deionized water.

2. Experimental

The typical synthesis procedure was as follows: 0.333 g CaCl_2 was dissolved in 50 mL ethanol in a conical flask and the solution was heated to 35°C in a water-bath. 30 mL 0.1 mol/L H_2SO_4 solution was added to the above solution accompanied by quick magnetic stirring. The solution was kept at 35°C for different times to form the products. After the reaction was completed, the resulting solid products were collected by centrifugation, washed with water and ethanol for several times to remove all impurities, and finally dried at 60°C in air. The effect of volume ratio of ethanol to deionized water was investigated.

X-ray powder diffraction (XRD) was collected on a Rigaku D/max 2550 V X-ray diffractometer with high-intensity $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) and a graphite monochromator. Morphology analysis of the samples was conducted on scanning electron microscopy (SEM, FEI-Sirion 200) and transmission electron microscopy (TEM, H-800 electron microscope, Hitachi).

3. Results and discussion

Figure 1 shows XRD patterns of samples prepared in mixed solvents of 50 mL ethanol and 30 mL water at 35°C for 1 min (figure 1(a)) and 30 min (figure 1(b)), respectively. The sample prepared at 1 min showed a mixed phase of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, JCPDS, Card No. 06–0046) and bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, JCPDS, Card No. 41–0224). The phase of bassanite was indicated as * in the corresponding XRD pattern (figure 1(a)). All the diffraction peaks can be indexed

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as monoclinic gypsum when the reaction time was 30 min (figure 1(b)). Compared to the standard pattern, no impurity peaks were found.

The morphology of CaSO_4 samples prepared at 35°C in mixed solvents of 50 mL ethanol and 30 mL water for different reaction times was characterized by FESEM, as shown in figure 2. The low magnification image (figure 2(a)) demonstrates that large-scale of CaSO_4 nanowires are produced by this facile method for 1 min. Higher

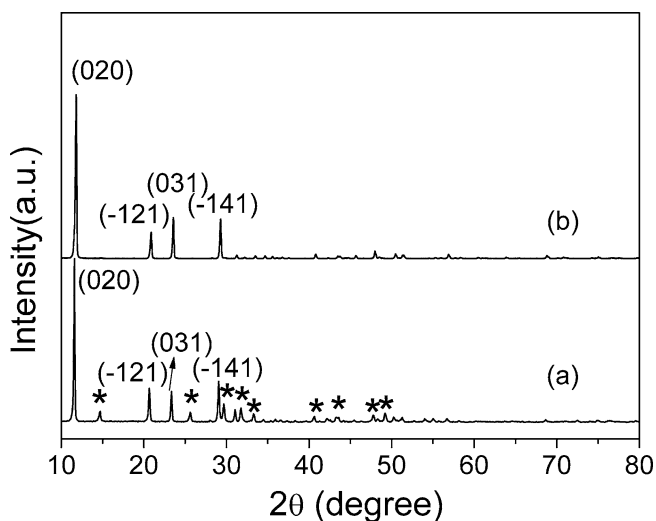


Figure 1. XRD pattern of sample prepared at 35°C for 0.5 h in mixed solvents of 50 mL ethanol and 30 mL H_2O .

magnification SEM image (figure 2(b)) clearly reveals that the CaSO_4 nanowires are relatively uniform. It is obvious that some of the nanowires are rolled from nanobelts, as we can see the rolling margin in figure 2(b). The thicknesses of the rolling belts are below 100 nm. Selected area electron diffraction (SAED) patterns taken from different positions from an individual nanowire or different nanowires were essentially the same. The inset of figure 2(b) shows corresponding SAED pattern of a single nanowire, indicating the single-crystalline structure of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ nanowires. When the reaction time was prolonged to about 0.5 h, the sample presented a mixed morphology of nanowires and nanobelts. Figures 2(c) and (d) show representative SEM images of this sample. The nanobelts have width of several micrometers and lengths of tens of micrometres. Further increasing the reaction time to 2 h, the product was mainly composed of sheets with irregular shape, as shown in figure 2(e). From a higher magnification image (figure 2(f)), we can see from the sheet surface that the sheets were constructed by the assembly of nanowires. The inset of figure 2(f) corresponds to SAED pattern of CaSO_4 sheet sample prepared at 35°C for 2 h, which also shows a single-crystalline diffraction pattern. In this case, the volume ratio of ethanol to water was adjusted to 78 mL/2 mL, 0.333 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 78 mL ethanol, and then 2 mL 1.5 mol/L H_2SO_4 solution was added to the above solution, while keeping the other procedures unchanged. The samples prepared at 35°C for 1 min and 2 h show almost similar nanorod morphology with a diameter of 50–120 nm and a length up to 1.5 μm (figure 3).

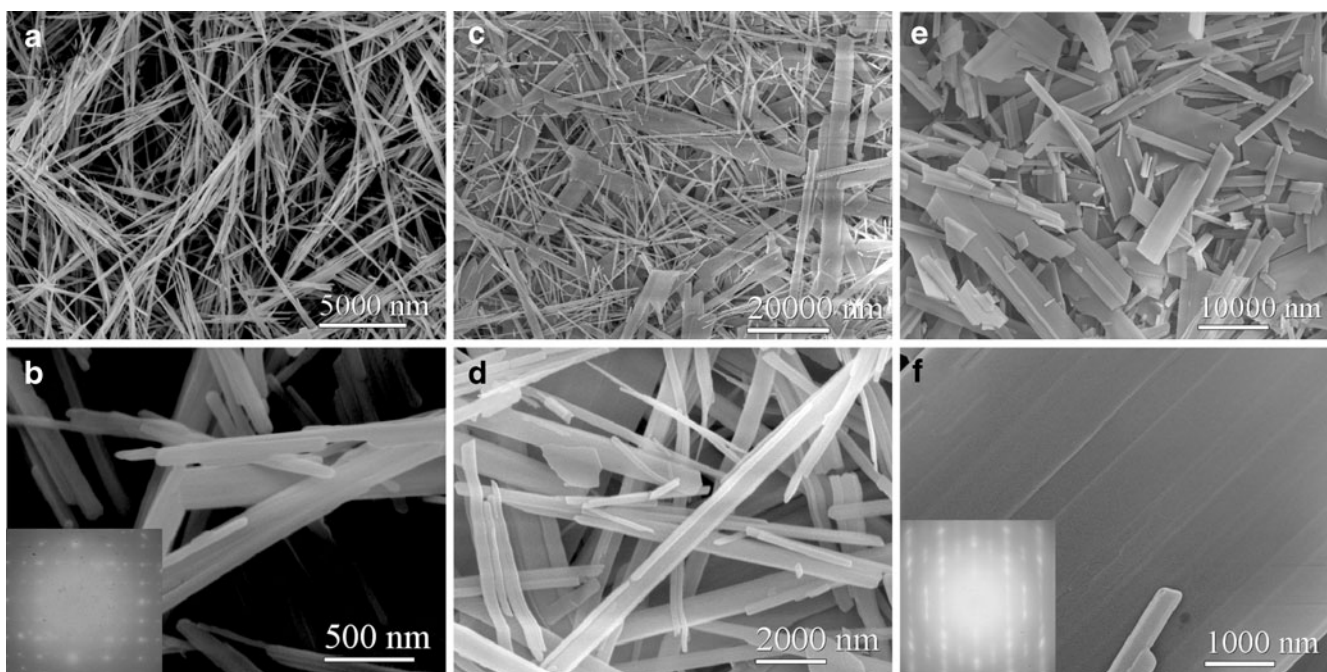


Figure 2. SEM images of CaSO_4 samples prepared at 35°C in mixed solvents of 50 mL ethanol and 30 mL H_2O for different reaction times: (a, b) 1 min; (c, d) 0.5 h; (e, f) 2 h, the insets of (b) and (f) are the corresponding SAED patterns.

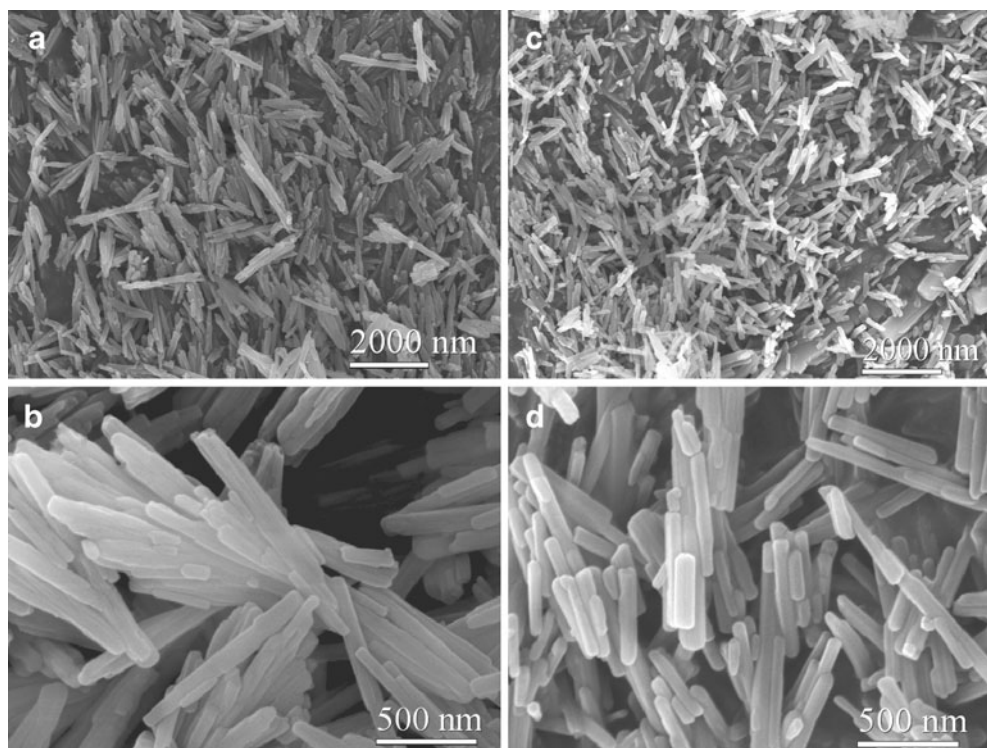


Figure 3. SEM images of CaSO_4 samples prepared at 35°C in mixed solvents of 78 mL ethanol and 2 mL H_2O for different reaction times: (a, b) 1 min; (c, d) 2 h.

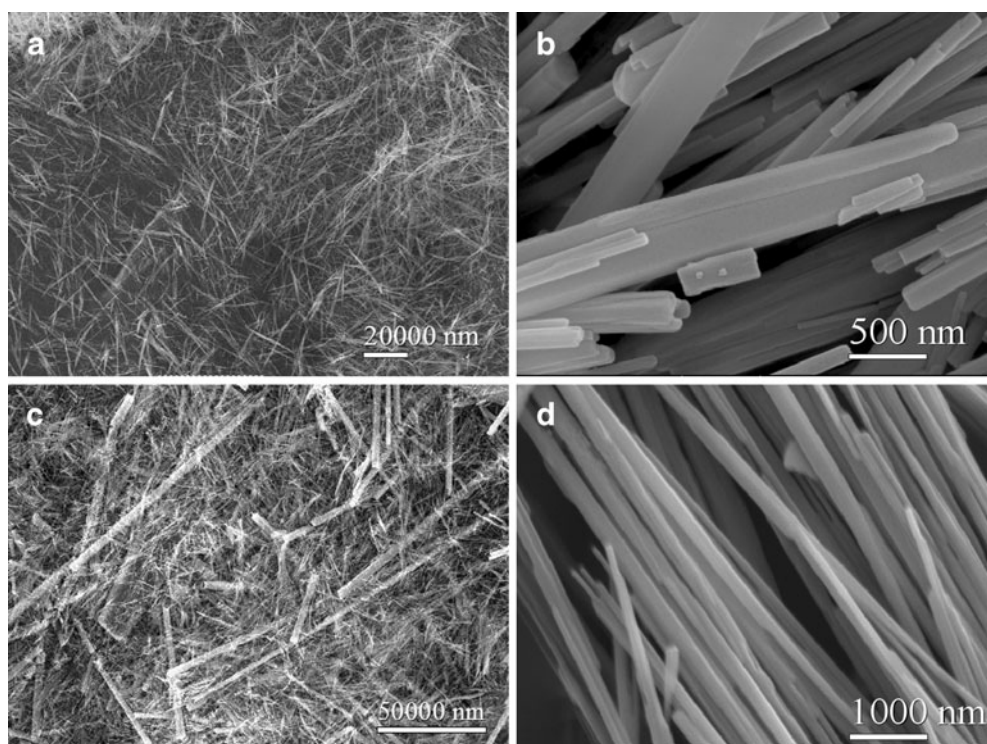


Figure 4. SEM images of CaSO_4 samples prepared at 35°C in mixed solvents of 50 mL DMF and 30 mL H_2O for different reaction times: (a, b) 1 min; (c, d) 2 h.

We also performed the experiments in which DMF was employed instead of ethanol in order to investigate the influence of different solvents on the formation of final products. The morphologies of CaSO_4 samples were investigated by FESEM. Figures 4(a) and (b) show the SEM micrograph of

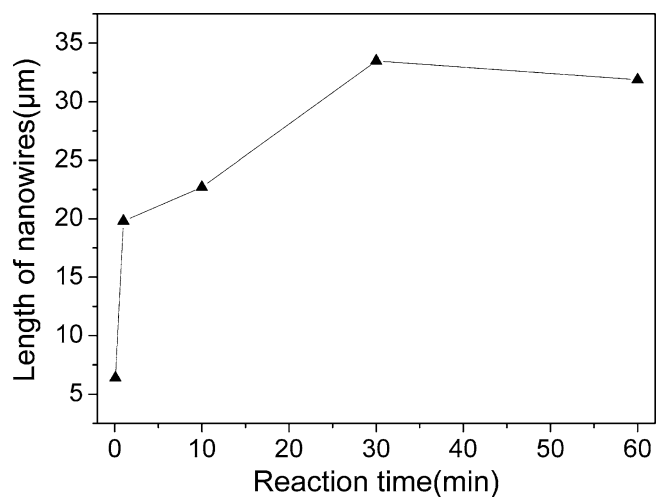


Figure 5. Effect of reaction time on lengths of nanowires in mixed solvent of 50 mL DMF and 30 mL H_2O .

sample synthesized at 35°C in the mixed solvents of 50 mL DMF and 30 mL water; one can see a large number of CaSO_4 nanorods/nanowires with diameter from 80 nm to 300 nm. When the reaction time was increased to about 2 h, large-scale nanowires were observed (figure 4(c)). However, certain amount of large micrometer rods/wires can be clearly seen. The nanowires have a length of tens of micrometres and a diameter of 80–200 nm as shown in figure 4(d).

As the reaction time has become one of the key parameters in determining the length and diameter of the obtained 1D structures, the length of these products has been measured via SEM images at 5 s, 1 min, 10 min, 30 min, 60 min and 120 min to capture the growth process of the wires. The calculated length of nanowires can be the average value of sixty nanowires lengths, as shown in figure 5. From this figure, one can see that the fast growth of the nanowires can be at the initial 1 min, the length of the product at 5 s can be about 6.4 μm, however, for the product at 1 min, this value can be about 20 μm. In the later stages for 10 min, 30 min and 60 min, the average values can be about 23 μm, 33.5 μm and 32 μm, respectively. From 1 min to 30 min, the nanowires had a tendency to grow more longer. However, after reaction for 30 min, longer time (60 min) can slightly be lowered to the lengths of the nanowires. When the reaction was 120 min, as we can see from figure 4(c), the monodisperse wires can be mixed wires of nanoscale and microscale. The microwires have a diameter of several micrometre, which can

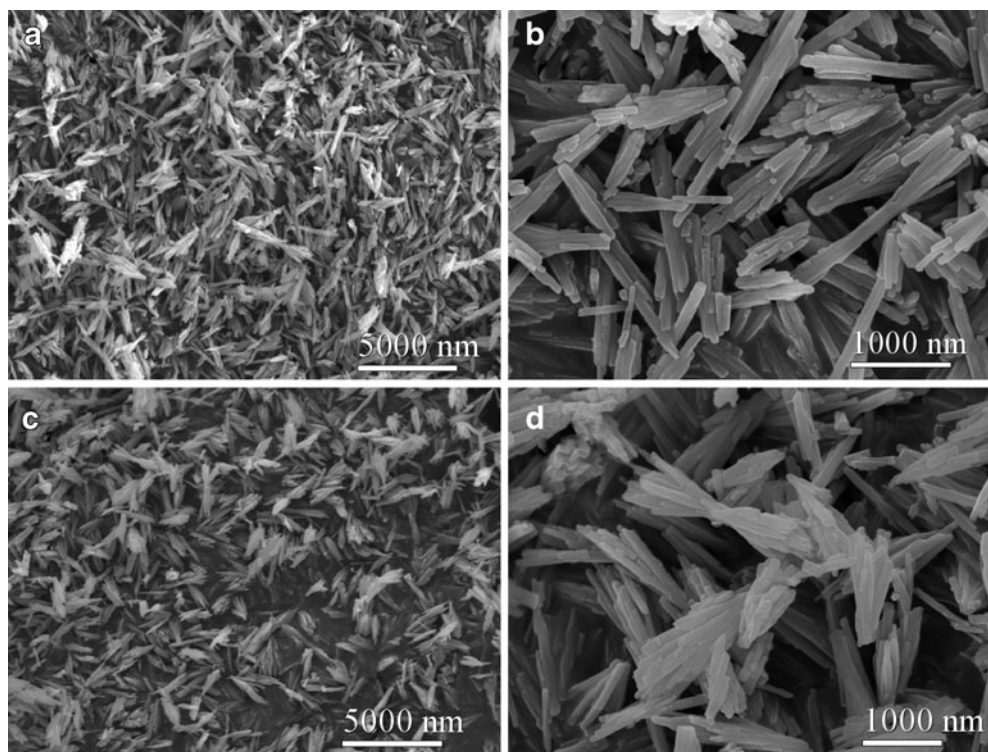


Figure 6. SEM images of CaSO_4 samples prepared at 35°C in mixed solvents of 78 mL DMF and 2 mL H_2O for different reaction times: (a,b) 1 min; (c,d) 2 h.

be explained by the dissolution of small nanowires and the growth of larger microwires. In this case, monodisperse and longer nanowires can be obtained at 35°C for 30 min.

Figures 6(a)–(d) are the images of samples prepared at 35°C in the mixed solvents of 78 mL DMF and 2 mL water. At the earlier reaction for 1 min, short nanorods were found as shown in figures 6(a) and (b). On increasing the reaction time to 2 h, no big difference was found as shown in figures 6(c)–(d), except that longer reaction time made the aggregation of nanorods to form straw-like bundles.

By comparing all the samples, the choice of solvent, volume ratio of organic to water and reaction time are the three major influencing parameters. For use of ethanol and DMF as the co-solvent, it is important that calcium sulfate has a smaller solubility in these solvents compared to deionized water, which is favourable for the precipitation of the product. Because of different chemical and physical properties, such as surface tension, viscosity and density, the morphology transformation process can be different.

4. Conclusions

In conclusion, we have successfully developed a new synthetic route for the preparation of well-crystallized calcium sulfate nanorods, nanowires, nanobelts and sheets in mixed solvents of ethanol/DMF and deionized water at a low temperature. By controlling reaction time, the choice of solvents and volume ratio of organic to water, CaSO₄ nanorods, nanowires, nanobelts and sheets are presented. The pro-

ducts obtained in this work also have potential applications in many fields, such as drug carriers.

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