

Continuous fabrication of calcium sulfate whiskers with adjustable aspect ratio in microdroplets

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Abstract:

Hemi-hydrate and anhydrous CaSO₄ whiskers with adjustable aspect ratio are **continuously** synthesized by the **reactive crystallization** of CaCl₂ to K₂S₂O₈ in microdroplets. The effects of solvent and reactive temperature are examined, with SEM and XRD characterizations. The results indicate that Hemi-hydrate and anhydrous CaSO₄ whiskers can be, respectively, obtained in aqueous and N,N-dimethylformamide solutions at 90 °C in 180 s. The addition of ethylene glycol or glycerol can lead to the increase in length and aspect ratio of the whiskers as well as increasing temperature. Thus this preparation technique can **continuously synthesize** CaSO₄ whiskers with two kinds of crystal structures **in a short time** and adjustable length and aspect ratios.

Keywords: CaSO₄, whiskers, crystal growth, crystal structure

1. Introduction

Calcium sulfate whiskers have been widely utilized as reinforcing materials in plastics [1], rubbers [2], paper[3] mills, and grafting materials in bone and tissue regeneration [4-5]. The three forms of calcium sulfate whiskers can be prepared in terms of dihydrate, hemi-hydrate and anhydrous CaSO_4 , Particularly, the last two forms attract much attention due to their excellent properties in thermal stability, chemical resistance and biocompatibility [6]. hemi-hydrate $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ whiskers can be prepared by dissolution-recrystallization [7-9], reactive crystallization [10-11], or microemulsion [12]. These methods always require long reaction time and/or high reaction temperature, consuming amounts of corrosive materials (crystal modifiers) and expensive surfactants. Anhydrous CaSO_4 whiskers are commonly obtained by energy-intensive calcination of dihydrate CaSO_4 at 400 °C, or through modifying Ca^{2+} with polymer ligands in organic solvents [13]. Furthermore, all these fabrications are carried out in batch operations, resulting in low production efficiency. It is highly demanded to develop a fast and continuous method to prepare both hemi-hydrate and anhydrous CaSO_4 whiskers.

Herein, we develop a facile and continuous technique to synthesize hemi-hydrate and anhydrous CaSO_4 whiskers with adjustable aspect ratio at low temperatures within several minutes. the morphology and the aspect ratio of the whiskers can be adjusted by Changing the solvent or temperature.

2. Experimental

Continuous fabrication of calcium sulfate whiskers is conducted in a home-made coaxial microfluidic device. two micro-needles ($\Phi 0.34$ mm in diameter) are assembled into a PTFE tube ($\Phi 1\text{mm} \times 400$ mm) which is immersed in a water bath [14]. Liquid paraffin is used as

continuous phase, and CaCl_2 and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, KPS) in different solvents as dispersed phase, such as N, N-dimethylformamide (DMF), ethylene glycol (EG), and glycerol (GL). Typically, 0.9 M CaCl_2 aqueous solution and 0.45 M KPS aqueous solution are prepared. The CaCl_2 and KPS solutions are pumped into two needles at a flow rate of 0.1 and 2 ml/h, respectively. Then the generated aqueous droplets are transported by continuous phase at a temperature of 90 °C and retention time of 180 s. The effluents are collected in a beaker precharged with petroleum ether, and the product is obtained after filtrating, washing with ethanol, and drying.

3. Result and discussion

The continuous fabrication of calcium sulfate whiskers is conducted by heating CaCl_2 and KPS microdroplets. The KPS is decomposed to release SO_4^{2-} , which subsequently react with Ca^{2+} to form calcium sulfate. the preparation is firstly carried out using aqueous solutions of CaCl_2 and KPS at 90 °C. The SEM picture of the resultant product (Fig 1a) reveals the formation of whiskers with the length of 1.62-10.33 μm and the width of 0.13-2.26 μm . The XRD pattern (Fig 2a) verifies the formation of hemi-hydrate CaSO_4 (JCPDS No.41-0224) with feature peaks at ???. However, the aspect ratio is relative low of only 2.5-18.7. we replace water with EG in the formation of KPS solution, as they can promote the growth of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers along the c axis [15]. The obtained product exhibits a XRD pattern in consistent with the standard peaks for $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (Fig 2a). The fibril-like morphology is shown in the SEM picture (Fig 1b). The length is 34.1-62.4 μm and the width is 0.26-0.67 μm , with the aspect ratio up to 49-127. Furthermor, we use GL to replace EG [16]. The similar results are obtained and the whisker-like crystals have The length of 27.2-56.7 μm and the width of 0.31-0.84 μm . the aspect ratio is 43-109, a bit less

than that using EG. These results suggest that $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers can be continuously prepared, and their aspect ratio can be adjusted.

As above the preparations use the aqueous solutions of CaCl_2 $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers are obtained. we replace water with DMF in the CaCl_2 solutions to prepare anhydrous CaSO_4 whiskers, which are more stable than $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers [6]. The SEM observation of the resulting product (Fig 1d) indicates that they exhibit rod-like morphology, with a length of 16.4-63.2 μm , a width of 1.2-6.2 μm and the aspect ratio of 13-32. The XRD pattern (Fig 2b) verifies the formation of anhydrous CaSO_4 (JCPDS No.43-0606), corresponding to the feature peaks at ???. We also substitute DMF with EG and GL in the KPS solution to prepare anhydrous CaSO_4 whiskers. The results indicate that the product with EG has a length of 24.3-59.5 μm , a width of 0.23-0.76 μm , and aspect ratio of 48-121 μm (Fig 1-e). In the case of GL in the KPS solution the length is 28.2-54.4 μm , width of 0.21-0.89 μm , and aspect ratio of 41-106 (Fig 1f).

In both aqueous and DMF solutions of CaCl_2 , EG in the KPS solution can result in the formation of whiskers with longer aspect ratios than GL. This can be ascribed to more hydroxyl groups in GL, which can restrain the growth of (001) facets. As the amount of hydroxyl groups is more than that to saturated adsorb on the (200), (400), and (220) facets, the extra hydroxyl groups may adsorb on the (001) facets of whiskers [15-16]. Besides, the viscosity of GL is higher than EG at the same temperature, which may suppress the interaction between hydroxyl group to Ca^{2+} and Ca^{2+} to SO_4^{2-} .

To examine the effect of temperature, we conduct the preparation using both DMF and aqueous solutions with GL at 50 °C and 70 °C, and compare the results with those prepared at 90 °C as shown above (Table 1). It is apparent that the length and aspect ratio of the whiskers

obtained from both solutions increase, with the increasing temperature while the width shows a reverse tendency. This can be explained by The fast decomposition of KPS at higher temperatures results in the increasing concentration of SO_4^{2-} in the reaction system. A high concentration leads to a high saturation degree, favoring the nucleation and growth of crystals. As the growth of the (200), (400), and (220) facets are inhibited by adsorption of GL, the growth in (001) facet is accelerated, thus leading to the increasing length and decreasing width [16].

Table 1 The calcium sulfate whiskers prepared at different temperatures

T/°C	Aqueous solution			DMF solution		
	Length(μm)	Width(μm)	Aspect ratio	Length(μm)	Width(μm)	Aspect ratio
50	17.5-45.6	0.55-2.32	18-37	15.4-43.7	0.94-3.16	12-29
70	24.5-50.2	0.47-1.27	29-64	19.6-49.6	0.78-1.86	26-57
90	27.2-56.7	0.31-0.84	43-109	28.2-54.4	0.21-0.89	41-106

4. Conclusion

We develop a continuous microfluidic technique for the preparation of calcium sulfate whiskers. Decomposition of KPS at high temperatures facilitate the releases of SO_4^{2-} , which reacts with Ca^{2+} to form CaSO_4 . $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and anhydrous CaSO_4 whiskers can be, respectively, prepared in aqueous and DMF solutions. The additions of EG and GL can significantly increase the aspect ratio of the resulting whiskers as well as the increasing temperature. The preparation time is less than 3 min, much shorter than those needed in batch operations. Such continuous process can remarkably enhance productivity and facile regulate the lengths and aspect ratios of CaSO_4 whiskers

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Figure captions:

Fig. 1 SEM images of the samples prepared in different solutions at 90 °C. CaCl₂ aqueous solution and KPS aqueous solution (a), KPS EG solution (b) and KPS GL solution (c); CaCl₂ and KPS DMF solutions (d), KPS EG solution (e) and GL solution (f).

Fig. 2 XRD patterns of the whiskers prepared in different solutions at 90 °C. (a) aqueous solution; (b) DMF solution.

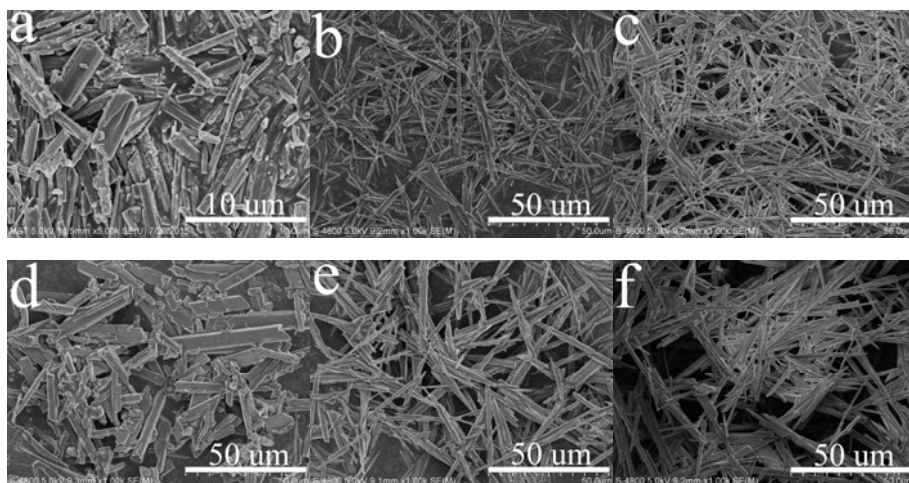


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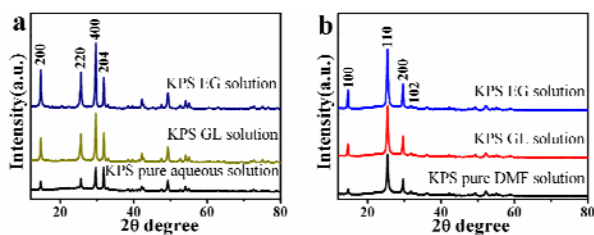


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