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A solid phase honey-like channel method for synthesizing urea-ammonium chloride cocrystals on industrial scale

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ABSTRACT

Unanticipated a new and simple urea-ammonium chloride cocrystal synthesis method on industrial scale was found during attempts to produce a kind of granulated compound fertilizer. The aggregation of fertilizer powder can make the interaction among particles from loose to close, which generate mechanical pressure and in turn act as the driving force to benefit cocrystal growth. Additionally, the honeycomb-like channels constructed by other coexisting compound make the water evaporates more moderate, which can help the formation of supersaturated solution at suitable rate, further promote the growth of cocrystal. This approach possibly opens a new route toward the developing methodologies for cocrystal synthesis.

Cocrystals appear as a class of new structurally homogeneous crystalline materials containing two or more components in definite stoichiometric amounts [1]. The design of cocrystals has been a field of intensive research as they have the potential to developing materials with desirable properties through modular approach [2]. Currently, established and proposed applications of cocrystals range from advanced pharmaceutical materials [3–5], molecular semiconductors [6], explosives [7] and luminescent materials [8] to media for stereocontrolled synthesis [9]. These applications undoubtedly depend on the cocrystal synthesis by mean of efficient and versatile methods. Despite the methods that evaporation [10], reaction [11], cooling crystallization [12], grinding [13], ultrasonic assisted [14] etc. have been reported for the production of cocrystals, they remained trial-and-error procedure and few of these technologies were immediately transferrable to an industrial process [15]. Therefore, it is necessary and critical to seek appropriate method for mass production so as to meet the need of practical application.

Recently, unanticipated, we found a new, simple, and high-yielding cocrystal synthesis method during attempts to produce a kind of granulated compound fertilizer. The starting materials urea, ammonium chloride, ammonium sulphate, potassium chloride, monoammonium phosphate, humic acid, and calcium sulphates were industrial raw material with the mass ratio of 143:214:322:71:107:71:71. During the production process, they were added to the mixer and stirred for 5 min firstly, then transferred to a 1.0 m diameter and 3.5 m long drum granulator rotating at 12 rpm [16], in which right amount of water (mass fraction 8%) were spayed by sprinkler systems and raw material agglomerate into 3 to 4 mm size granular fertilizer. The feeding rate was 3 t per h and the total granulation process took about 10 min in environment temperature. After surface drying and sieving, the around ball shape fertilizer particles (Fig. 1A) were packed in plastic bags, seal kept at room temperature and ambient pressure. One month later, a large number of needle-like crystals, ca. 3 mm, appeared (Fig. 1B). X-ray diffraction (XRD) analysis [17] revealed that the crystal is a fully ordered urea-ammonium chloride cocrystal, which crystallizes in the orthorhombic space group Pmna (53) and exhibits a one-dimensional layer-type structure along *y* axis and two-dimensional network structure. CCDC 1434837 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre. Literature survey shows this is a cocrystal with the same composition and completely different structural characteristics compared with that previously synthesized in laboratory [18].

Both urea and urea cocrystals have been the subject of extensive theoretical and experimental study in the past three decades, mainly because of their interesting physical and chemical properties [19]. Here, a method for industrial-scale production of urea-ammonium chloride cocrystals was provided with merits such as convenient operation and mild condition. Moreover, the products could be easily separated from the byproduct according to their density by means of wind winnowing method. In its simplest form

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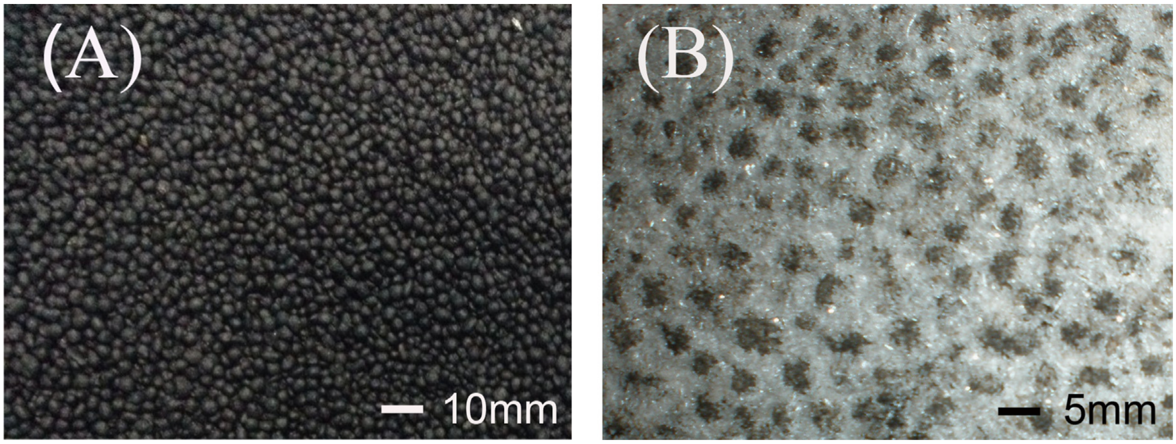

Fig. 1. The obtained fertilizer particles (A) and generated urea-ammonium chloride cocrystal (B). Images were taken using Olympus digital camera.

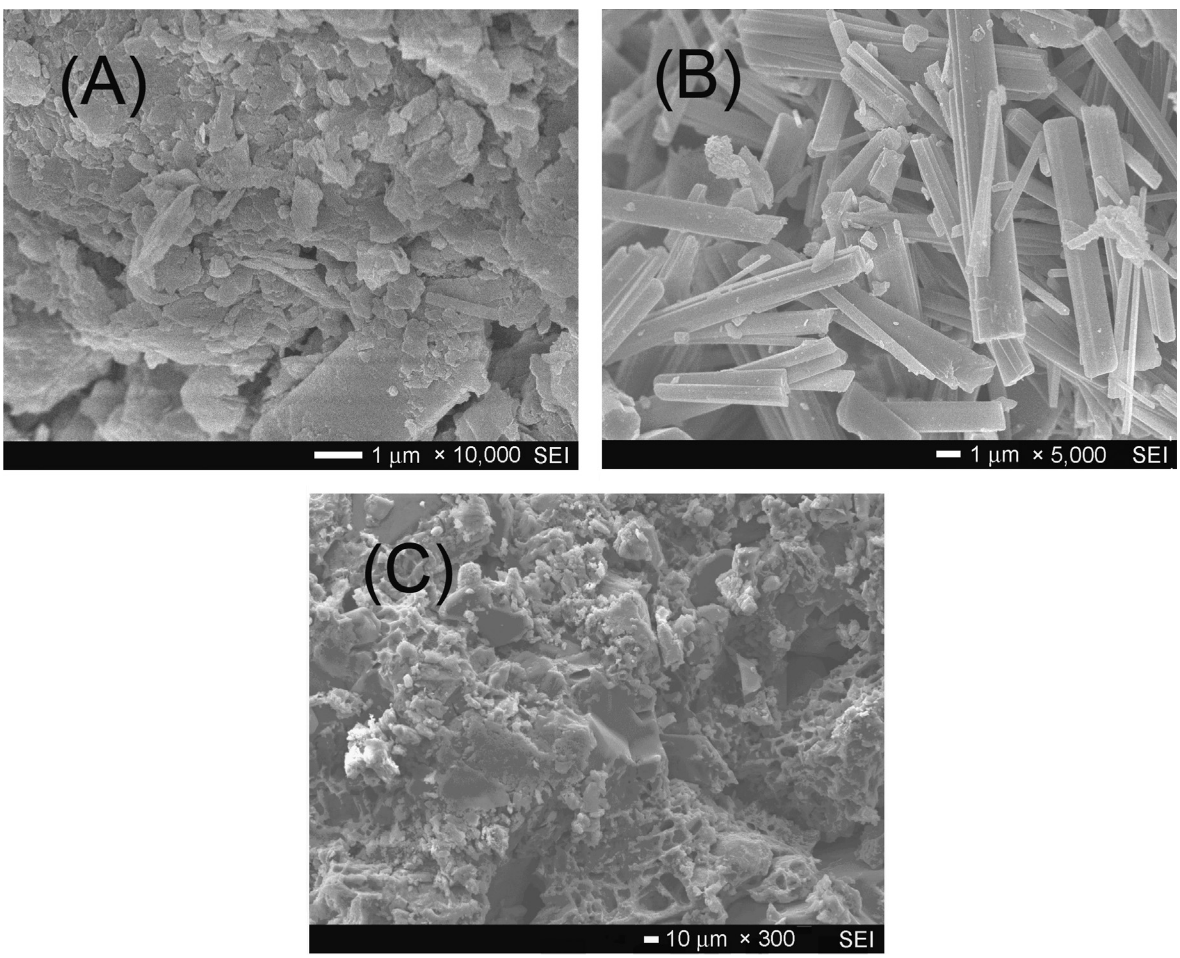

Fig. 2. The SEM images of humic acid (A), calcium sulphate (B) and fertilizer particle (C).

it involves throwing the mixture into the air so that the wind blows away the lighter cocrystals while the fertilizer granules fall back down.

To investigate the inner cause for the cocrystal growth, the microstructure of raw material and fertilizer particles were characterized by scanning electron microscope (SEM) respectively. Results analysis show that humic acid and calcium sulphate play important role. Before fertilizer granulation, the humic acid is lamellar (Fig. 2A) and the calcium sulphate is rod-shaped (Fig. 2B). After the granulation process, humic acid and calcium sulphate formed a honeycomb-like microstructure (Fig. 2C). This porous channel was thought to make the water evaporates more moderate, which can help the formation of supersaturated solution in small space at a suitable rate. Additionally, the process converting powder materials into larger compacted agglomerates make the interactions between materials from loose to close. The mechanical pressure resulted from the compaction are considered as the driving force to main cocrystal growth.

The obtained urea-ammonium chloride cocrystals are typical ionic cocrystals (ICCs), and they can be regarded as three-