

Controllably Constructing morphology and structure of potassium chloride crystal by green supersaturation modulation

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ABSTRACT

Controllable and green construction of morphology and structure in potassium chloride (KCl) crystals is necessary in the fields of pharmaceuticals, catalysis, minerals, and jewels design. Here, the work presented a lucid way for preparing KCl crystal with various morphology including hopper-, sphere- and hollow cube-like structure through green supersaturation modulation. Parameters including stirring speed, cooling range, cooling rate, and excess inorganic composing ions influenced the growth kinetics of hopper KCl crystal as well as the surficial morphology and structure: (1) Metastable region and stable conditions were beneficial for uniform growth of crystal; (2) Small size of crystal particles were obtained with high shear force; (3) Corner angle of crystal would be abraded in slow cooling rate; (4) Non-uniform crystal appeared in improper cooling range condition; (5) Additional composing ions might introduce deformed structure according to the basic crystal repeating unit with corresponding elements. Based on the above study of growth kinetics, hopper-, sphere- and hollow cube-like crystal were obtained. The morphology and structure properties of various crystal were researched by three-dimensional visualization, X-ray diffraction (XRD), and scanning electron microscope (SEM) for optimized application such as higher exposing surface area of hopper-like crystal than original cubic crystal. The main exposed faces for smooth cubic, hollow cubic, and hopper structure exhibited were (200), (220), and (400) facet, respectively, which could be a consequence of the inner beveling. Surface of spherical structure was a circular arc with relative high roughness, being ascribed to the formation mechanism of spherical structure from cubic structure. Therefore, the work presented a strategy to controllably design KCl crystal with different structure and morphology in a green way.

1. Introduction

Crystals lie everywhere near us not only as natural ones like snowflakes, ice, diamonds, or other gemstones but also artificial crystals were also precisely designed to ignite their great potential as nutrients, necessities and even treatment for disasters [1–3]. For centuries, they have been playing an essential role in amazing variety of forms such as salt [4], pharmaceuticals [5], micronutrient delivery [6], minerals [7] and many other fields [8].

As main resource of element potassium, which is essential for plants growing [9], Potassium chloride (KCl) has been designed with certain

physical and chemical properties for being widely applied in different fields, leather making, explosives, porcelain, fertilizer, phosphors, and medicines [10–12]. For instance, hygroscopic properties of KCl are reported to be closely related with effect of climate [13]. Besides, enhanced optical- simulated luminescence response of KCl aerosol was beneficial for regeneration effect in the materials of detector [14–16]. Improving mechanical properties of KCl was helpful for warehousing, transporting, and storage process to far-abroad countries [17]. What's more, served as carrier, KCl could be used to strengthen UV emission lines for generation of photo electronic devices [18,19]. The nature of crystals shows vital effects in their function [20,21], therefore, it is of

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high necessity to controllably synthesize crystal with many morphology and surficial properties to ignite their promising applications [22].

The design of growing crystals has been a challenge to all researchers [23,24]. Different methods like specific solvent especially organic solvent method [25–27], additives method [28,29] and extreme heat & pressure method [30–32] are thought to be well-known ways to yield new structures of crystals. Besides, tons of efforts were attempted to synthesize diverse property of crystals [33,34]. However, chemistry reagents pollution has been posing great threat to human society in all sorts of aspects including drinking water, food industry, and even clothing contact. Demanding of eliminating the undesirable chemistry additives is urgent in social activities.

To some extent, only aimed morphology and exposure faces could bring the desired effects. In general, the natural crystallographic habits are known to be rarely influenced by normal conditions due to the crystallization thermodynamic equilibrium, while the crystal structural, morphological as well as surficial properties may differ depending on crystallization kinetics [35]. By repeating the basic structure along different paths, orientation and quantities, the crystals may end up with parallelism, misaligned spiral growth, or secondary nucleation. Let along that in nature, the crystals are rarely found to be in their equilibrium form which requires steep conditions. The basic repeating unit finally pile up to form varied macroscopically crystals which is also known as crystal clusters that may seem far dissimilar from the ideal perfect structure, but the latter appears in a more common way.

It's of significant scientific and technological importance to investigate the method to design crystals without additives thus to pave an environmentally friendly path to the applications of industrial crystals. Hence, the phenomenon that crystal always grow in form of clusters sheds some new light to the controllable crystal design by only modulating the general conditions like crystallization rate, supersaturation, and temperature. In this work, as one of the most significant crystals in nature an actual application, KCl was taking as an example to research the strategies of controllable construction of crystals. The solubility of KCl highly depends on temperature of solution, ensuring the possibility of precise regulation of the oversaturation of salt thus to modulate crystals during the cooling process. Batch experiments were performed to research how the cooling method would affect the morphology, surficial properties of KCl crystal. This work aims to help understand the controllable design of crystals by supersaturation modulation, not only salts but also medicine crystals, minerals, jewels and semi-soluble minerals.

2. Experimental section

2.1. Materials

Saturated saline solutions were prepared with analytical pure grade KCl reagents from Sinopharm Chemical Reagent Co., Ltd., China, and Milli-Q deionized water (Millipore SAS, France) with a resistivity of 18.2 M Ω •cm, thus to minimize the disturbance of impurity ions. Hydrochloric acid, potassium hydroxide, nitric acid, potassium nitrate, ammonia and ammonium chloride with analytical purity were all purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Each experiment was performed with a fresh solution according to the solubility of KCl in water under different temperature conditions. To realize the additive-free reaction, the weighted KCl reagents were directly used as seeds.

2.2. Samples preparation

After crystallization, the grown KCl samples were immediately filtered by diameter of 0.22 μ m filter paper after each crystallization experiment in order to avoid the further growth. Afterwards crystals were kept in an oven at 45 °C overnight to dry up for other measurements.

2.3. Experimental design

A designed vertical cylindrical jacketed crystallizer with 250 mL capacity combined with mechanical stirring machine and a double blade parallel stir bar with length of 2 cm was performed, where warm water bath was provided by a constant speed programmable thermostatic bath (XOYS-2010 N, ATPIO Ltd., Nanjing, China) to realize an accurate modulation with minimal configuration of 0.01 °C. By means of modulating cooling range, cooling rate and reaction period of water bath, the KCl crystals with different morphology were grown in the crystallizer.

In a typical batch cooling crystallization process, 100 mL of saturated KCl solution at 30 °C was added into the chamber of crystallizer and proper stirring speed was performed to ensure an ideal mixture of the solid-liquid system. Subsequently, the warm bath with 35 °C was set in advance for 30 min to keep all water cycle path warm enough to ensure the later saline clear, i.e., no existence of solid salt. Typical cooling program was set to cool the saturated KCl solution of 30 °C down to 27 °C within certain period, where the filtration device was kept in an oven at 27 °C before the program ended to minimize the further growth of KCl crystals during the sample drying process.

For parameter impacts experiments, the cooling programming was well designed to realize the modulation of cooling range and rate by setting different temperature and reacting time, where the former was set to be same range as 3 °C but different starting temperature as 24, 27, 30 and 33 °C without any other changes from typical cooling process. For cooling rate impactor, the cooling range was set to be 30–27 °C to emit the influence of environmental temperature condition with various cooling period from 15 to 300 min (cooling rate from 12 °C/h to 0.6 °C/h), where the longer the cooling period meant a lower cooling rate. For stirring speed parameter, increasing speed as 100, 200, 300, 400, 500, and 600 rpm were applied for the system while all other condition was kept the same with typical cooling experiment. In additive impacts experiments, low dosage as 0.01 % and 2 % in column (in this case with 100 mL saturate solution, 0.01 mL and 2.0 mL of addition was added) was chosen to research about the extra ions' influence on crystallization.

2.4. Characterization

The morphology of shape and surface property of grown crystal was observed by a stereoscope and SEM (Phenom ProX G6, Netherlands), respectively. Crystal structure of samples was detected using XRD with Cu K α radiation (Bruker AXS, Germany).

3. Results and discussion

3.1. Supersaturation controlled crystallization

As a common method of mixing as well as energy input for reactions, stirring not only helps the system unbalanced but also provides a certain level of mixing effect, especially for multi-phase systems like solid-fluid mixture. The energy input increases with higher stirring speed. To figure out the relationship between stirring speed and the morphology of crystal, batch crystallization experiment of cooling process with different speed including 100, 200, 300, 400, 500, and 600 rpm was performed and the results were shown in Fig. 1a-d and Fig. S1.

Intuitively, the size of crystal reached a good distribution in hopper-like size under 400 rpm condition. With lower stirring speed (100, 200, and 300 rpm), the crystals showed hopper structure but in unevenly size and shape distribution, while small crystal pieces tended to be broken from the bigger hopper structure under high rotational speed (500 and 600 rpm). The crystallization process usually requires a gentle solution environment, i.e., a proper mix ability of the crystal-saline system. The homogeneous morphology of crystal in Fig. 1c demonstrated that this system well fitted the mixing purpose under 400 rpm. The mechanism could ascribe to the suspension critical speed N_t calculation according to

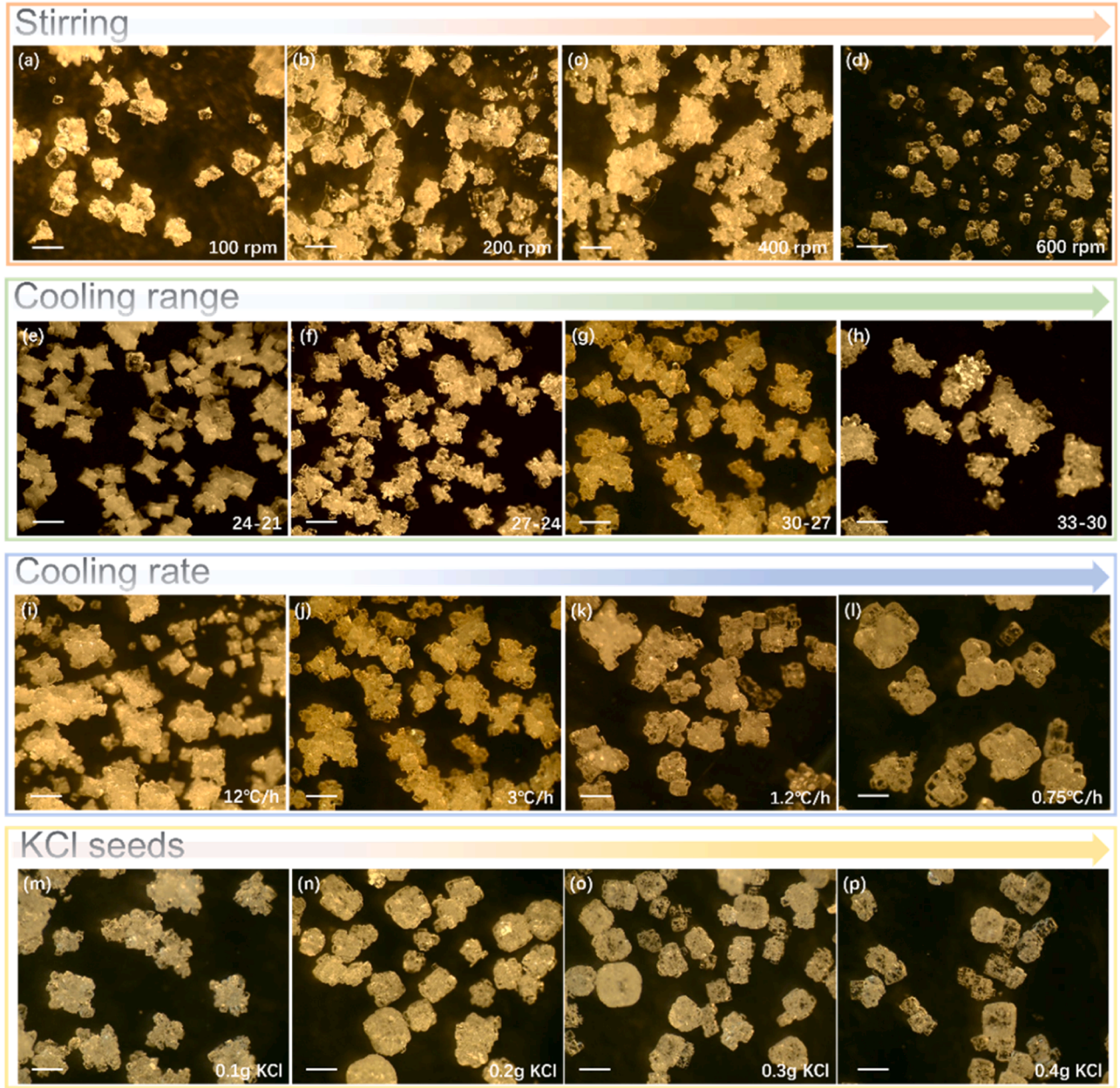


Fig. 1. Effect of conditional parameters for KCl crystal grown through batch cooling experiments: Effect of stirring speed on crystal grown, (a) 100, (b) 200, (c) 400, and (d) 600 rpm from 30 °C to 27 °C in 60 min; Effect of cooling range on crystal grown, (e) 24–21 °C, (f) 27–24 °C, (g) 30–27 °C, and (h) 33–30 °C (with cooling period of 60 min); Effect of cooling rate on crystal grown, (i) 12 °C/h, (j) 3 °C/h, (k) 1.2 °C/h and (l) 0.75 °C/h from 30 °C to 27 °C with 400 rpm; Effect of additive seeds amount on crystal grown, (m) 0.1 g, (n) 0.2 g, (o) 0.3 g, and (p) 0.4 g. Scale bar=500 μm.

Pavlushenko's formula:

$$Nt = 0.105 \frac{g^{0.6} \rho_D^{0.8} d_p^{0.4} D^{1.9}}{\mu^{0.2} \rho^{0.6} d^{2.5}} \quad (1)$$

With Nt the suspension critical speed of mixer (revolutions per second, rps); g the acceleration of gravity in m/s^2 ; ρ_D and ρ the density of solid-state particles and liquid-state solution in $kg \cdot s^2/m^4$, respectively; μ the viscosity of the fluid being mixed in $Kg \cdot s/m^2$; d , D and d_p the diameter of mixer, mixing vessel, and grown crystal in m, respectively. Based on the equation, the Nt would be 5.69 rps, i.e., 391 rpm, close to the experimental result 400 rpm. The satisfied distribution of hopper-like crystals came from the well mixed solid-liquid system, while the higher stirring speed offered redundant energy for crystallization, thus destroying the hopper structures to small pieces in Fig. S1b.

The phenomenon that solubility of KCl is subject to changes in

temperature, as mentioned above, gives an insight of the idea that the hopper structure may change under different cooling range. Batch cooling experiments of 3 °C within ranges of 24–21 °C, 27–24 °C and 33–30 °C were set to see the morphological differences of crystals from that of 30–27 °C crystals. As shown in Fig. 1e-h, the crystals in different conditions all exhibited hopper-like structure but diverse size distribution. In Fig. 1e, the inner cubic owned a relatively large length attached with eight much smaller branches on corners. However, in Fig. 1f and g, the size of branches on corners were better developed thus those crystals showed obvious hands with almost non-existent inner cubic structure. The different shapes could be well explained by various growing strategies that as shown in Fig. S2, there will be three main growing directions on one cubic structure-from center to corner (green), along edge (yellow) and perpendicular to square face (pink) with a declined growing rate (vice versa during resolving process). During

crystallization, it's obvious that corners are immersed in large area of saturation KCl with abundant K/Cl ions to help grow. On edges, there will be relatively less chances to contact with saturated solution while on faces, ions possessed the least saturated KCl solution. It could be inferred that the greater growing rate difference between corner and face direction occurred under increasing temperature conditions. In other words, when the temperature was set to be low, the (200) face of KCl crystals tended to grow which required a gentle environment, thus benefiting the formation of inner cubic structure. On the contrary, if the temperature was high, the difference of growing rate between corner and face direction was magnified that the growth along corner direction was better promoted than on face direction. The corners of primary small cubic became the secondary nucleation sites for later cubic. Consequently, the branches on eight corners got preferentially developed and the final crystals showed a hopper-like structure. Notably, according to the Oswald Ripening theory, dissolution and nucleation occurred during the crystal growing process. The temperature condition is a key parameter of the balance of these two reactions, improper condition might bring on non-uniform crystals. As demonstrated in Fig. 1f, g and h, the best size distribution occurred under proper temperature condition (in Fig. 1g, 30–27 °C), while 1f and 1h displayed small pieces and oversized aggregations. Thus, the proper cooling range of hopper-like KCl crystals should be set as 30–27 °C.

Apart from cooling range, the cooling rate is another key factor of the grown hopper-like structure. Solubility of KCl highly depends the temperature, thus the cooling way offers oversaturation of crystallization. The cooling rate greatly affected the oversaturation thus induced the change in growing speed of crystals. To research the correlation between cooling rate and morphology of crystals, in this work, various cooling rate as 12.0, 3, 1.2 and 0.76 °C/h. Obviously, the lower cooling rate offered a steadier growing environment for KCl crystals. Representative results were shown in Fig. 1i–l and others in Fig. S3 with same evolution law.

Crystals in figures showed the revolution trend from hopper-like structure with distinct cubic corners to spherical particles. In Fig. 1i, the crystals were in different size but the same hopper-like morphology, which should be ascribed to the proper oversaturation as well as Oswald ripening theory as mentioned above. With the slower cooling rate, the crystals got a relative peaceful grow to display an even size distribution as in Fig. 1j and k. However, the latter result exhibited a hopper-like structure with better developed branches compared to the former. This structure could be inferred that at the very beginning of cooling stage, the saline kept clear without crystal seeds formation due to the supersaturation of KCl under 25 °C. Burst of nucleation happened only when the real oversaturation exceeded that value. Immediately followed a fast growth, and dissolution of some KCl seeds, thus helped formation of the inner hopper structure. Later, however, with a steady cooling environment with 1.2 °C/h in Fig. 1k, the branches obtained chances to show an ideal development as big cubic. With a slower cooling rate in Fig. 1l at 0.75 °C/h, the branches achieved a better grow as well as attrition on the surface of cubic corners where the latter phenomenon usually occurred with long enough crystallization process. As a result, the crystals showed an aggregation with several spherical small particles. Among which some remained a hopper-like structure with 8 spherical small particles as displayed on upper left corner in Fig. 1l, illustrating the similar growing mechanism as above results.

One other impactor involved was the additive seeds that always pertained great influence on the morphology of crystals. Analyzed grade of KCl was used as an environment-friendly additive without non-necessary substance to study the influence on cooling experiments. The original reagent pertained a rough surface as shown in Fig. S4. Limited amounts including 0.1, 0.2, 0.3, and 0.4 g KCl was added into the saturated salinity at 30 °C and the results were displayed in Fig. 1m, n, o and p. It's clear that crystals showed an even distribution and discrepancy from reagent morphology with only 0.1 g additive seeds, while big size particle with a spherical shape remained with more seeds,

indicating the possibility of adjusting crystal morphology and shape distribution with low amount of original reagent. Inferred was the mechanism that additive seeds helped breaking the balance of saturated solution, dissolve, and growth of KCl occurred on surface of seeds at the same time, thus to help average the morphology of grown crystals. However, excessive seeds aggravated the crystallization of KCl on surface of seeds but the dissolve was restrained thus reserved those big particles in reagent. As a consequence, proper amount of crystal seeds would help with modulating morphology of grown crystals with the dynamic adjustment between dissolve and crystallization of the additive seeds.

3.2. Crystal products

3.2.1. Hopper-like structure

As a typical FCC (Face-centered cubic) type crystal, a standard basic KCl crystal would grow to be a cubic structure with sharp corners. In this work, the grown crystal by cooling method showed a hopper like structure, as shown in the inserted picture in Fig. S5. The special anisotropic structure could be attributed to the faster growth on corners and edges than the centers of its faces. Before the core cubic grow as a bigger cubic, the eight corners turned to be the site of secondary nucleation, then the corners of secondary cubic became the sites of ternary nucleation, and so on, thus to form a hopper-like structure with higher exposure of crystal face area in comparison with basic cubic structure, as illustrated in the inserted pictures in Fig. S5. Their corresponding X-ray diffraction (XRD) results demonstrated that they exhibited similar crystal faces but the hopper structure crystal pertained much stronger diffracted intensity, indicating the success of high exposing crystal faces area of the hopper-like structure. Notably, the connected part between two "steps" might be the extra crystal face (220) and (222), in consistent with XRD result. Aided by the multi-staged structure, the hopper-like crystal exhibited greater surface area than that of a cubic crystal.

Based on results above, the different growing rates of lattice plane contributed to the various appearances with the same hopper-like structure. To further unveil the influence of common cooling parameters, series of batch experiments were applied here to study the different shapes of KCl crystals by additive-free method.

Demonstrated above was the phenomenon that the KCl crystals tended to show a hopper-like structure during the cooling process in proper range and rate. Nevertheless, the evolution of this special structure remained unclear which should be an interesting part to help understanding the mechanism. In this part, the beginning temperature of solution and cooling rate were set to be 30 °C and 3 °C/h based on previous research to get the uniform hopper-like structure, thus the different crystallization period should be the only factor to influence the crystals. By collecting crystals of those batch experiments, evolution of hopper-like structure would be easily unveiled as shown in Fig. 2.

It's clear that at the first stage of crystallization as in Fig. 2a, hopper-structure appeared in a rough and frizzy way, indicating the fast nucleation with high supersaturation as mentioned before. Meanwhile, those crystals with thin and underdeveloped branches ended up in aggregations due to their high surficial energies. As time elapsed, the branches of crystals in Fig. 2b acquired the chance to further grow to exhibit less sharp structure, ensuring the hopper-like structure with a better distribution. By comparing Fig. 2b, c and d, there was a tendency that the crystals kept in a form composing of 8 small units but increasing sphericity. Growth as well as attribution were thought to be the main mechanisms of this phenomenon. More detailed revolution results were displayed in Fig. S6, with the similar conclusion illustrated by those typical morphologies.

3.2.2. Sphere-like crystals

Normally, the perfect cubic structure exhibited six foursquare faces as the surface, coming with the high possibility of cohesion, thus

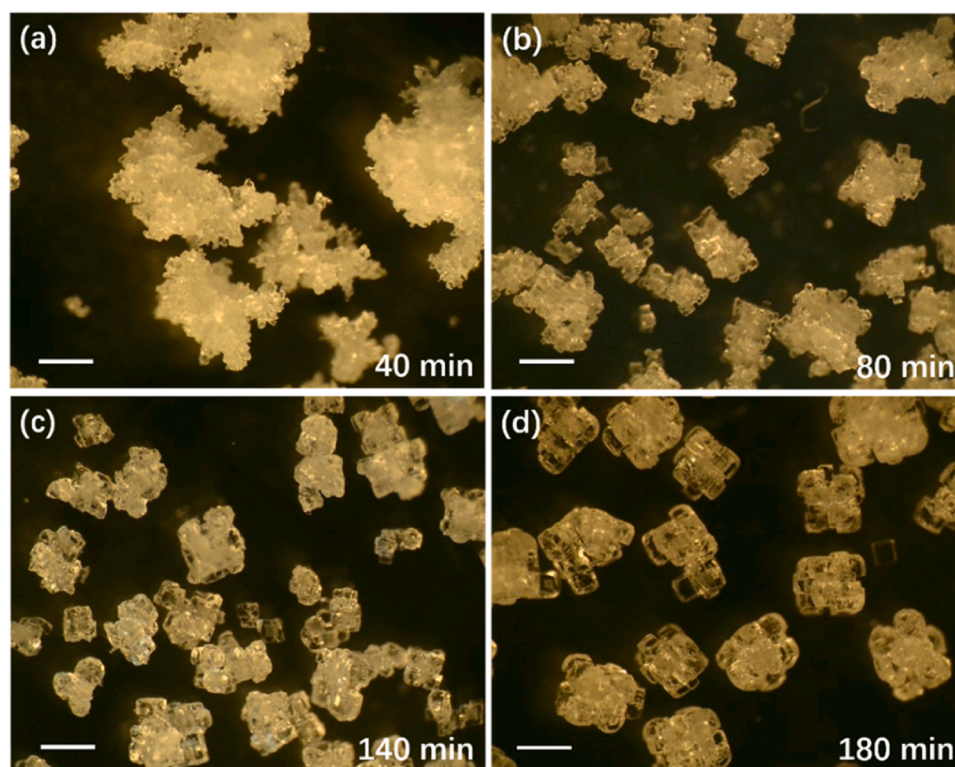


Fig. 2. Stereoscopic results of KCl crystals grown by batch cooling experiments from 30 °C for increasing period with cooling rate at 3 °C/h, scale bar=500 μ m.

hindered the separation of crystals during production transfer process and got medicine invalidated. Though by cooling method, superficial area of produced hopper-like crystal increased by the stackable growth of cubic units but remained the foursquare surface. Therefore, efforts have been made to grow crystals with special shapes to avoid clusters formation. It's known that the morphology of crystal production shows an important role in the transportation process as well as application. One of the most favored shape of crystals is spherical structure with low possibility of aggregation. Nevertheless, it's hard to change the intrinsic propriety of crystals at ambitious temperature and pressure without additives. Hence, in this part, only the spherical-like structure of KCl crystals by abrasion from cubic habit was studied to help understand the evolution of cubic-to-spheric crystal.

Shown in Fig. 3 was the evolution of aspheric KCl crystals. During the cooling experiments, a greater value of cooling range between 40 and 30 °C was set to get a better morphology of crystals to help research the evolution process. Similar to the conclusions in Fig. 1i, j, k, l and Fig. S3, the former crystals displayed a hopper-like structure as in Fig. 3a, b c and also d, demonstrating a common phenomenon during cooling process. However, in Fig. 3e, the units of a hopper structure became smooth to form a bigger cluster. Notably, the eight units as the branches of a hopper structure got chance to grow completely as cubic formation to form a bigger cubic with obvious crossing lines in the center. Besides, due to the Oswald ripening, some crystals were dissolving and others growing, thus showing in various size distribution. With a slower growing rate in Fig. 3f, the limited ions tend to form crystals only in relative greater size, single cubic-like crystals with crossing lines could also be found. Similar conclusion appeared in slower cooling rate as shown in Fig. 3g and h. The final crystal in Fig. 3i pertained a spherical morphology of size over 500 μ m with smooth surfaces, indicating the tendency of increasing size and smoothness with smaller cooling rate. Apart from cooling rate, the evolution of the spherical crystal in Fig. 3i (i.e., cooling rate at 1 °C/h) was also studied as shown in Fig. S7. Cubic crystals with crossing lines pertain a great percentage in Fig. S7c, then they got abraded to show spherical surfaces instead of well-cubic forms.

Finally, as time elapsed, the cubic crystal with eight smaller cubic units turned to show a whole structure with spherical structure in Fig. S7f [22]. The quantity of KCl crystals displayed a decreasing trend here which could be ascribed to the Ostwald Ripening theory that small pieces of crystals would dissolve to form bigger crystal due to the difference of ions concentration near surface of crystals.

3.2.3. Hollow cube-like crystals

Demonstrated was that the crystals shapes are affected by adding extra ions that might also introduce impurities thus lower the production qualities. Interestingly, the composing ions of crystals in solution may show influences on the final shape. Taking KCl for example, the structure of KCl is face-centered cubic, indicating the repeating unit consisted by K and Cl element with ratio of 1:1 as shown in Fig. 4. Actually, there are many types of foreign chemical like NaCl, MgCl₂ and K₂SO₄ during industrial manufacture process of extracting KCl from salt-lake, and plentiful attention has been stressed to research the impacts of Na⁺, Mg²⁺ and SO₄²⁻ which is not the main content in this discussion but only the two constituent ions of KCl. Moreover, the pH of solution is not always at 7 which means extra H⁺ or OH⁻ ions, for example, flotation of KCl was always conducted under pH~6 by using octadecylamine hydrochloride as collector [36–38]. (Surface chemistry features in the flotation of KCl) In this section, to understand how excess K or Cl ions in solution will influence the KCl crystals shapes, certain quantities of KOH and HCl was added into the solution and cooling process was performed.

Shown in Fig. 4 are the results of KCl crystals with 0.1 %, 2 % addition of KOH and 0.1 % and 2 % addition of HCl during crystallization procedure. Interestingly, the morphologies of Fig. 4a and 4d shared the similar hopper-like structure but different details of branches. Here, the KOH and HCl were thought to be original of only K/Cl ions since OH⁻/H⁺ ions with 0.1 % and 2 % dosage were later found to be not working as effective factors during crystallization. With limited extra K ions, the small units of hopper structure showed more spherical shape, indicating the importance of K ions as the face centered member of cubic structure. This phenomenon was further demonstrated in Fig. 4b that

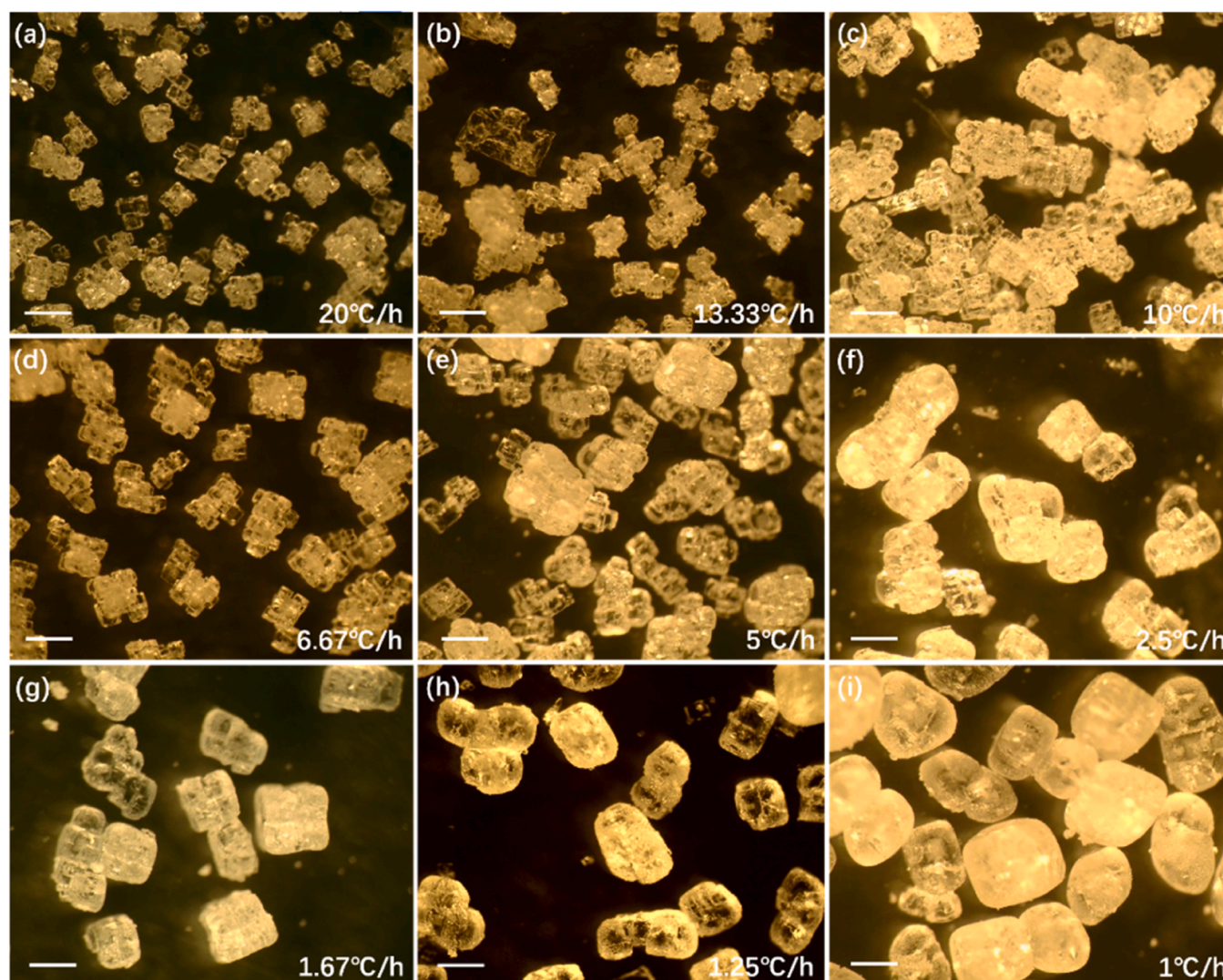


Fig. 3. Stereoscopic results of KCl crystals grown by batch cooling experiments from 40 °C to 30 °C with decreasing cooling rate at 20, 13.33, 10, 6.67, 5, 2.5, 1.67, 1.25 and 1 °C/h. Scale bar=500 μ m.

when excessive K ions were added in solution for longer period and full reaction, the cubic structure of KCl maintained with smooth edges on prisms of cubic structure. According to the atomic structure diagram in Fig. 4c, the K atoms occupied the center of each prism with Cl atom as corner atom, thus helping formation of structure by 12 K atoms as structure of cubic without sharp corners (Cl atoms). In Fig. 4d, when small amount addition of Cl ions was applied, crystals also exhibited hopper structure with thin arms on eight corners, while they grew to get connected by a framework structure with more Cl ions in Fig. 4e. The phenomenon should be explained by the same mechanism above that connected Cl atoms on corners promised the structure of prisms. Notably, the deformation of crystallization habit requires restrict conditions which promises KCl crystals with cubic-like structure under constant temperature and pressure. For the cooling process with extra K or Cl ions, the abundant adding ions would work as frames of cubic-like structure, thus exhibiting crystals as smooth cubic with K element at center on prisms or hollow cubic with Cl ions at corners as illustration in Fig. 4f.

It's worth noting that to exclude the OH^- and H^+ ions impacts, additive ions NH_4Cl , KNO_3 , HNO_3 and $\text{NH}_3\cdot\text{H}_2\text{O}$ were also applied to batch cooling crystallization of KCl as shown in Fig. S8 with dosage as 0.1 % and S9 as 2 %. It could be concluded that extra HNO_3 and $\text{NH}_3\cdot\text{H}_2\text{O}$ had limited influence on the shape of KCl crystals as hopper structure.

However, with additive NH_4Cl in Fig. S8a and S9a, both low and high dosage yield KCl crystal with well-grown branches from 8 corners, similar with results with extra HCl. With 0.1 % and 2 % extra KNO_3 in Fig. S8b and S9b, both KCl crystals possessed cubic form with relatively perfect shape. The shapes of these crystals were not in excellent coincidence with that with extra HCl and KOH, it could be ascribed to the minor impact of NH_4^+ and NO_3^- ions. Here, the supplementary results only aimed to help understand the extra composing K and Cl ions' influence on KCl crystals. The above results further demonstrated the idea of modulating crystallization based on intrinsic repeating unit of KCl crystals.

3.3. Structural and surficial properties

3.3.1. Structure

Based on above work, various morphology of KCl crystal have been prepared including hollow cubic, smooth cubic, hopper and sphere KCl crystals as shown in inserted pictures in Fig. 5, along with their corresponding XRD results that all of them showed high purity and crystallinity. It's clear that smooth cubic structure contains high percentage of (200) face while hollow cubic relatively more (220) face which could be a consequence of the inner beveling. For hopper structure, the abundant complicating exposing area displayed extra (222) faces. Limited faces of

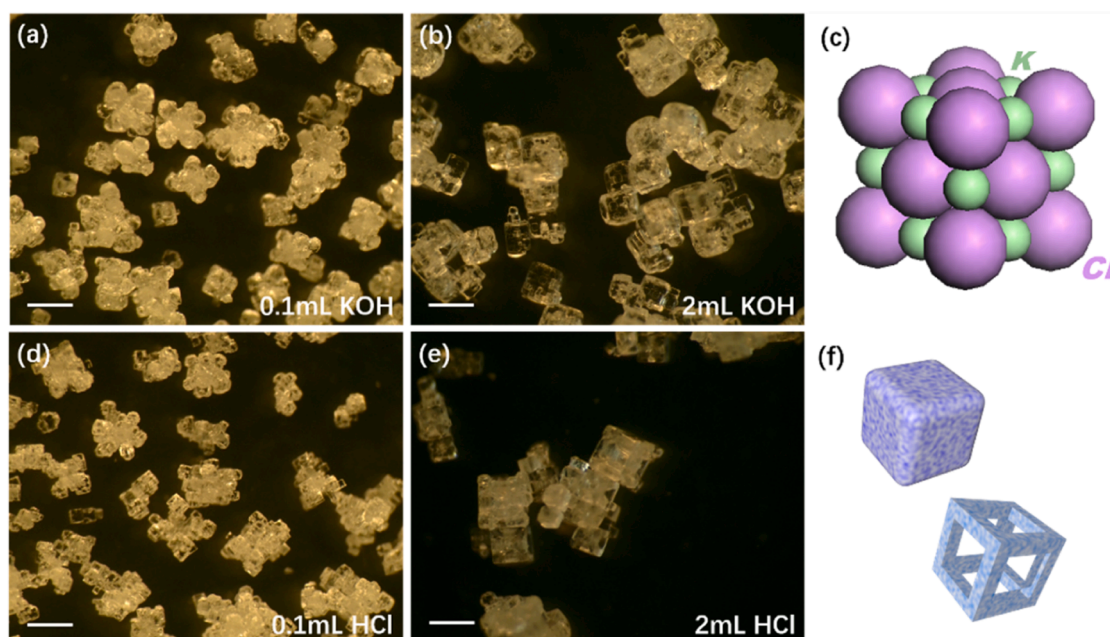


Fig. 4. Stereoscopic results of KCl crystals grown by batch cooling experiments from 30 to 27 °C with existence of 0.1 mL of KOH (a) and HCl (d), and 1 mL of KOH (b) and HCl (e) from 30 to 23 °C for 700 min, especially. Scale bar=500 μm. Atomic illustration of KCl with Cl (c) or K (f) as center atom.

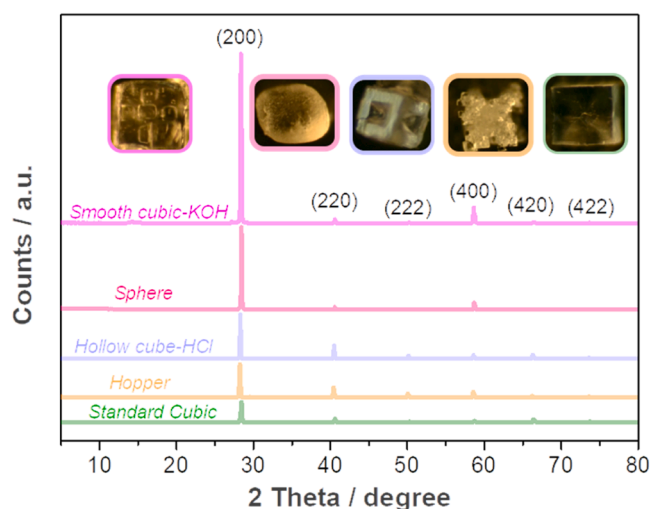


Fig. 5. XRD results of smooth cubic with KOH, sphere, hollow cube with HCl, hopper and standard cubic KCl structure, and corresponding stereoscopic results.

(200) and (400) were shown in sphere structure due to its isotropy. In conclusion, various shape with special exposing area would contribute to the different intensity of crystal faces, promising their further applications related to the properties of exposing faces.

3.3.2. Roughness

Aimed shapes prepared above guaranteed them with special structures for wilder application but the surficial morphology of grown crystals remained unveiled. Here, SEM combined with three-dimensional graph was performed to help understand the surficial properties as shown in Fig. 6. SEM and their corresponding three-dimensional results of smooth cubic with KOH additive in Fig. 6a and b showed a relative flat surface on the cubic part, with a smooth corner instead of sharp one, indicating the preferred formation of foursquare face rather than prisms. The surface of spherical structure in Fig. 6c and

d exhibited a circular arc with relative high roughness which could be ascribed to the formation mechanism of spherical structure from cubic structure as explained above. For hollow cubic structure in Fig. 6e and f with addition of HCl, prisms with sharp corners remained with a four-square hole on center of the six faces of one cubic structure. Similarly, hopper structure in Fig. 6g and h showed holes in center of each face, with eight branches on direction of corners. On the contrary, the original basic cubic of KCl structure in Fig. 6i and j displayed rather flat surfaces due to the well crystallization.

4. Conclusions

In summary, a green and controllable approach was proposed for preparation of various structure and morphology of KCl through supersaturation modulation. Hopper -, sphere- and hollow cube-like crystals were obtained in the work. The parameters including stirring speed, additive seeds, pH condition, cooling range and rate in the supersaturation modulation technology were well researched and explained. At certain condition, the crystal would grow in a uniform state, otherwise, they would form as small pieces, abrasion of crystals, etc. Different products were analyzed in the structure, morphology and surficial property. Three-dimensional visualization was applied in detecting roughness and appearance of crystal. The main exposed faces for smooth cubic, hollow cubic, and hopper structure were (200), (220), and (400) facet, respectively, which could be a consequence of the inner beveling. Spherical structure surface showed a higher roughness than the others, which was originated from the formation mechanism of spherical structure to cubic structure. Herein, the work developed an environment-friendly method to prepare different crystal structure for application as template, flotation, and others.

CRediT authorship contribution statement

Yuan Yuan: Writing – original draft, Methodology, Formal analysis, Investigation. **Wei Quan Zhan:** Supervision, Formal analysis. **Wei Zhang:** Methodology. **Ruoyu Yao:** Software. **Peng Chen:** Investigation. **Feifei Jia:** Data curation. **Hao Yi:** Supervision. **Shaoxian Song:** Formal analysis. **Alejandro López Valdivieso:** Formal analysis.

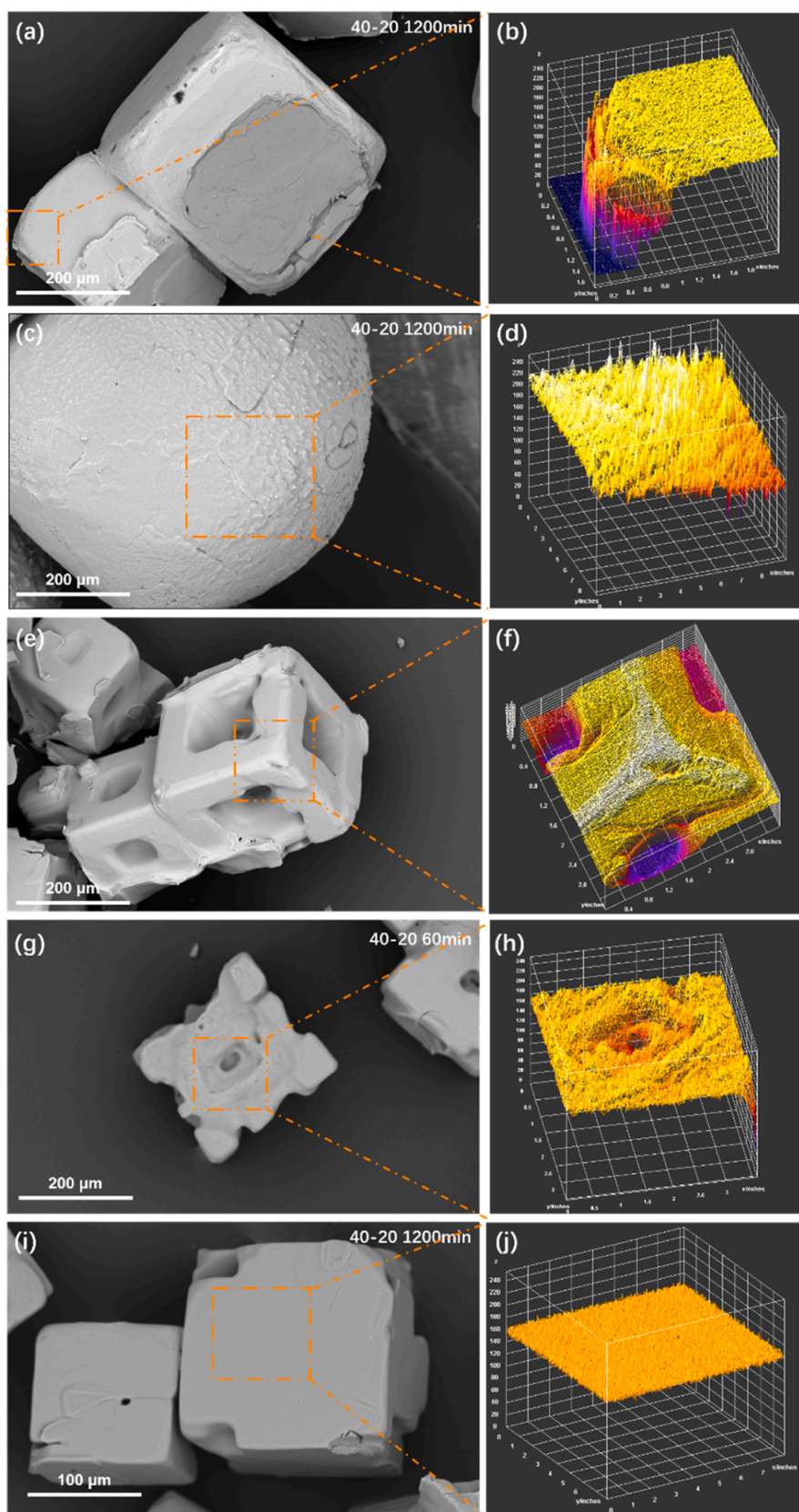


Fig. 6. SEM results of smooth cubic with KOH, sphere, hollow cube with HCl, hopper and standard cubic KCl structure, and their surficial 3D plot results.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.surf.2024.104973](https://doi.org/10.1016/j.surf.2024.104973).

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