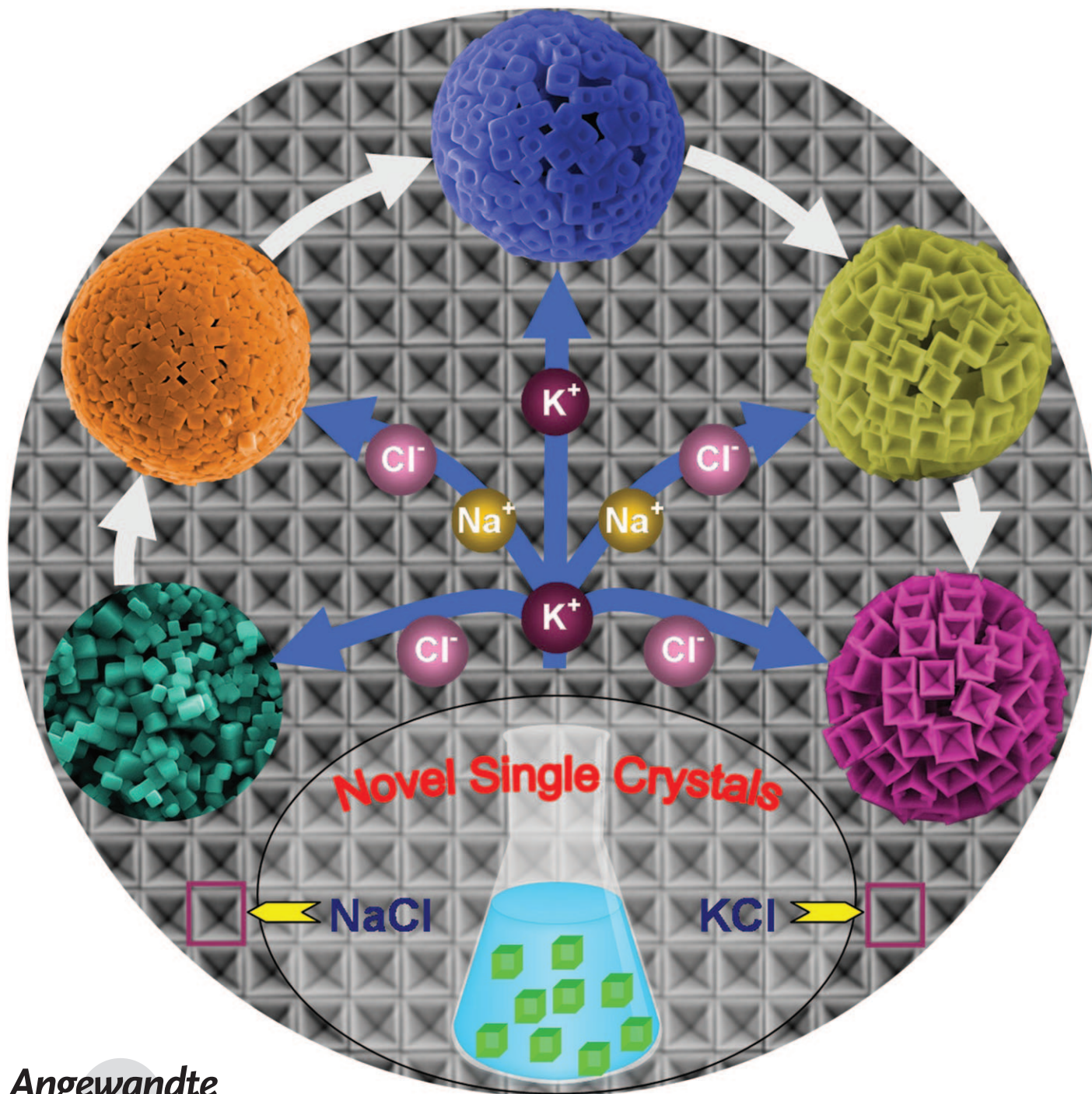


Hopper-Like Single Crystals of Sodium Chloride Grown at the Interface of Metastable Water Droplets**

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Intrinsic shapes of inorganic crystals are produced under equilibrium thermodynamic and kinetic conditions, which is due to the relative order of surface energy at different crystallographic planes.^[1] During the evolution in shapes, the lower-energy planes grow while the higher energy planes disappear, and this process can be modified when the surface energy at certain plane is altered or the growth along certain direction is hindered.^[2] Currently, organic ligands or additives have been widely used to control/tune the growth rate of different planes in aqueous solutions for the formation of various nanostructures and polyhedrons.^[3–5] In combination with the control of organic ligands/additives, interfacial growth at air/liquid, liquid/liquid, or solid/liquid interfaces is a promising alternative to complex heterogeneous and hierarchical architectures.^[6] Such results give us a general impression that these approaches are successful in the control of crystallographic morphology of water-insoluble compounds, such as metals, oxides, sulfides, and insoluble salts.^[7–9] On the other hand, water-soluble salts as a large family of inorganic compounds have recently been explored for the production of heterogeneous crystalline shapes and structures by controlling the evaporation of saturated aqueous solution, but their intrinsic crystal growth is hardly changed.^[10–13] The impressive structures/architectures have rarely been reported.

Sodium chloride and potassium chloride are the most representative examples of water-soluble salts that always appear in the form of highly regular cubes in both natural and artificial environments.^[14,15] A change in their intrinsic growth nature for the production of other shapes and structures has not yet been achieved, but is very important for the understanding of growth mechanism of various crystals. Herein, we report the hopper-like single crystals of NaCl and KCl and their self-assembly at interface of metastable water microdroplets. In a typical experiment, cyclohexane (8 mL) was first mixed with acetone (20 mL) and then agitated for 30 min at room temperature. A aqueous NaCl solution (1M, 7.5 μ L) was subsequently injected into the above organic mixture through a syringe pinhole (25 μ m diameter) under vigorous agitation. After 10 min, the white NaCl precipitates were

collected by the removal of supernatant. The identical procedure was also used for the preparation of KCl crystals.

The structure and composition of the products, confirmed by means of X-ray diffraction (XRD) measurement, are face-centered cubic NaCl with phase purity (JCPDS, 89-3615; Supporting Information, Figure S1). The NaCl precipitates consist of microparticles, most of which are in the size range 10–40 μ m, as revealed by scanning electron microscopy (SEM; Figure 1 a). Individual particles have a highly spherical

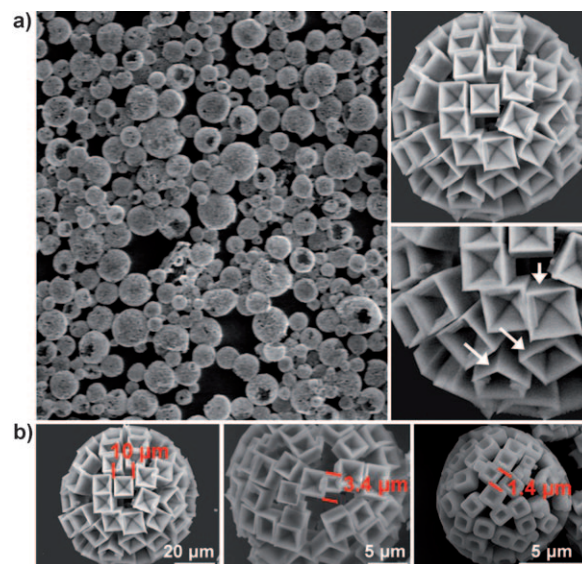


Figure 1. a) Overview SEM image of NaCl spherulites with hollow spherical architecture. The high-magnification SEM images (upper and lower insets) show that the NaCl hollow microspheres are built up of blocks of cubic hopper-like single crystals. b) SEM images showing the sizes of hopper-like crystal blocks at hollow microspheres with different diameters. (See the text for further details.)

shape and hollow interior, thus suggesting the growth of NaCl at the interface between water microdroplets and the mixing organic phase. Surprisingly, cubic hopper-like single crystals appeared when one of the single microspheres was further magnified (upper inset of Figure 1 a). The hollow microspheres were completely built up of tens of uniform hopper-like single crystals with a size of about 10 μ m. With a further magnification, it can be clearly seen that every individual crystal has one deep rectangle hole open toward the outside of the sphere, but the highly regular cubic shape with equal dimensions and sharp edges is still maintained (as indicated with arrows in the bottom inset of Figure 1 a). The same microspheres and hopper-like single crystals were also observed for KCl (Supporting Information, Figure S2).

The hopper-like crystals have very similar size in an identical hollow microsphere, but the building blocks at different hollow microspheres have different sizes. As shown in Figure 1 b, the sizes of hopper-like crystal blocks are 10, 3.4, and 1.4 μ m in three microspheres with diameters of 68, 23, and 10 μ m, respectively. Because the sizes of water microdroplets dispersed in the organic phase have a relatively wide distribution, the larger interfacial area of large droplets must lead to the formation of more nuclei at this interface of

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organic solvent/water. As NaCl concentration in all droplets is the same, the density n of nuclei at the interfaces of different-sized droplets is very similar. Thus, the size of single crystal block can be estimated as $V_{\text{crystal}} = (c(4/3)\pi R^3)/\rho(n \times 4\pi R^2) = cR/3\rho n$, where c , R , and ρ are the concentration of NaCl, the radius of microdroplet, and the density of NaCl, respectively. This equation reveals that the crystal blocks become smaller with the decrease of size of hollow microspheres.

The mechanisms of NaCl crystal growth and microsphere formation were proposed and further demonstrated by tuning the experimental conditions and monitoring the intermediate products (Figure 2). Detailed experiments reveal that the

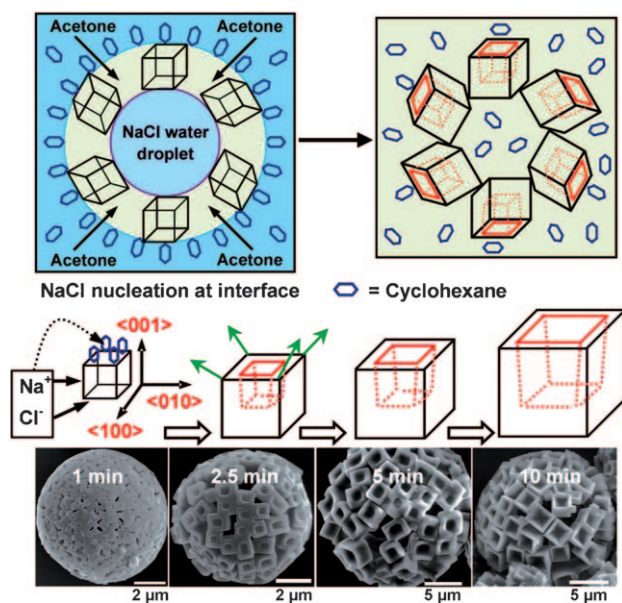


Figure 2. Mechanisms for the formation of metastable water microdroplets, NaCl nucleation at the interface, and the growth process of cubic hopper-like single crystals. The SEM images (bottom) show the time-dependent evolution of NaCl crystal morphology.

absence of cyclohexane leads to the formation of normal cubic NaCl crystallites, and neither hopper-like shape nor spherical architecture was observed (Supporting Information, Figure S3), suggesting the crucial role of cyclohexane for the formations of hollow spherical architecture and hopper-like single crystals. Cyclohexane is completely compatible with acetone, but incompatible with water (phase diagram in the Supporting Information, Figure S4). On the other hand, acetone is compatible with water, and as such, the presence of cyclohexane can temporally stabilize the water microdroplets by reducing the diffusion rate of acetone into water droplets, as shown in Figure 2. Such formation of metastable water microdroplets provides an unconventional environment for the unique growth of hopper-like crystals. The slow diffusion of acetone into water droplets results in the supersaturation of NaCl and the initial nucleation at the surface of water droplets. The NaCl nutrient from the water droplets is sustainably supplied for the uniform growth of NaCl single crystals. Meanwhile, the cyclohexane molecules contacting with the {001} plane toward organic phase prevent the growth

at this {001} direction. However, the growth of other {001} planes and the {111} planes maintained the original growth rates. As a result, the cubic hopper-like single crystals and their uniform arrangement in the form of hollow microspheres were achieved.

Furthermore, the growth of the hopper-like crystals may also be related to the diffusion rate of the ions and the growth rate of the crystals based on the concentration gradient around the interface of metastable water microdroplets. Experimentally, the ions for crystal growth were continuously supplied from the water microdroplets. At the areas in/near the water microdroplets, the rate of the ion diffusion is relatively fast with respect to that of crystal growth, and the concentration of ions is relatively uniform in/near the water microdroplets. Growth takes place at the entire crystal surfaces controlled by the crystal growth rate, giving rise to a normal cube. At the areas far from the water microdroplets (the faces of the crystals toward outside), the rate of diffusion is relatively slow with respect to the growth rate, and the growth becomes diffusion-limited.^[9] The concentration of ions is largely decreased close to the centers of the crystal faces toward outside, which may lead to the preferential growth of sidewalls and give rise to hopper-like crystals.

More experimental observations have been performed to confirm the critical role of the nonpolar species in the formation of hollow spherical structure and hopper-like NaCl cube: a) when *n*-hexane replaced cyclohexane in the synthesis, similar hopper-like NaCl cubes in the arrangement of hollow microspheres were also obtained; b) the use of *n*-pentanol, with a polar hydroxy group, led to the NaCl cubes with a small/shallow pit open toward outside; c) when cyclohexane was replaced by cyclohexylamine with basic amino groups, hollow NaCl microspheres were produced, but normal NaCl cubes rather than hopper-like ones were observed at the microspheres (Supporting Information, Figure S5–S7).

The most direct evidence for the above growth process was obtained by monitoring the evolution of intermediate products by SEM (the bottom images of Figure 2). At the initial stage (1 minute), hollow microsphere composed of small regular NaCl cubes appeared. With the increase of growth period to 2.5 minutes, a single pit was formed on every cubic block. Subsequently, the pits developed into larger and deeper holes with the growth of NaCl cubes after 5 minutes. Finally, the hopper-like single crystals and their uniform arrangement in the form of hollow microsphere were formed (10 minutes). As another strong support, the hopper-like hole became smaller and smaller and finally disappeared with the decrease of cyclohexane dose from 8 mL to 0.1 mL (Figure 3), which further confirms the above growth mechanisms. More experimental observations, including the effects of temperatures, are given in detail in the Supporting Information.

In summary, we have developed a new strategy of exploiting metastable water droplets to control the growth and assembly of water-soluble inorganic salts. The interfacial interaction between nonpolar species and crystal surface can successfully change the growth nature of water-soluble salts, and an unexpected structure and morphology was produced that had not previously been achieved by traditional

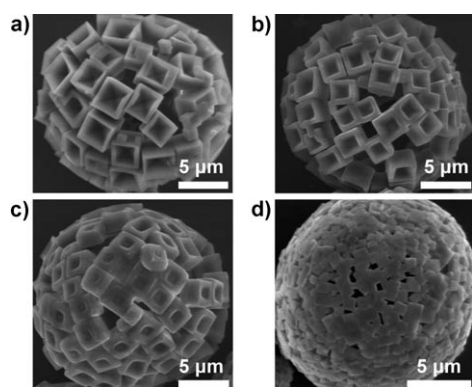


Figure 3. Evolution of NaCl crystal shapes with decreasing volumes of cyclohexane: a) 8.0, b) 4.0, c) 0.4, d) 0.1 mL. All of the samples were collected after stirring for 10 min.

approaches. The method and mechanism of this report may be extended to the control of crystallization and assembly of other water-soluble compounds.

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