Electronic Supplementary Information (ESI)

Utilization of charged microdroplets for the controlled rapid synthesis of hollow sodium chloride single crystals

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1. Experimental section

Chemicals

Sodium chloride (NaCl, AR, Sinopharm Chemical Reagent Co., Ltd.). Potassium chloride (KCl, AR, Sinopharm Chemical Reagent Co., Ltd.). Nitrogen gas (99.99%, Fuzhou Xinhang Industrial Gas Co., Ltd.). Silicon wafer (500 μm in thickness, single-sided polishing, Zhejiang Lijing Optoelectronics Technology Co., Ltd.). Deionized water (DI water, 18.2 MΩ) was prepared from Millipore Direct-Q 3 UV.

Electrospray setup

The electrospray setup mainly consists of a high voltage power (0-30 kV, BOHER), a syringe pump (Harvard Apparatus), a syringe (500 μL, Hamilton), a fused silica capillary tubing (50 μm in inner diameter, 150 μm in outer diameter, 20 cm in length, Zhengzhou Innosep Scientific Co., Ltd.), a two-way union (1/16 inch, Swagelock), a tee (1/16 inch, Swagelock).

Preparation of saturated NaCl solution

8 g NaCl was added into 15 mL DI water, followed by thorough stirring at room temperature (20 ℃). Subsequently, the saturated solution was filtered to collect the filtrate. The pore size of the filter is 0.22 μm.

Preparation of saturated KCl solution

8 g KCl was added into 15 mL DI water, followed by thorough stirring at room temperature (20 ℃). Subsequently, the saturated solution was filtered to collect the filtrate. The pore size of the filter is 0.22 μm.

Preparation of NaCl crystals

Crystallization is a complex process influenced by various environmental factors. The solubility of NaCl in water exhibits minimal variation with temperature changes across the range of 0 to 100 ℃ (Fig. S3). Consequently, we have chosen to maintain a constant temperature of 20 ℃ for our experiments. In the context of the microdroplet method, numerous factors can affect NaCl crystallization, including solution flow rate, inner diameter of the capillary, spray time, sheath gas pressure, high voltage value (HV), height (H, defined as the distance between the capillary tip and the substrate), and environmental relative humidity (RH). Given the multitude of variables and their potential equivalent effects, we have opted to keep specific values constant for the first four variables: 10 μL min^{-1} for solution flow rate, 50 μm for inner capillary diameter, 5 s for spraying time, and 4 bar for sheath gas pressure. Our primary focus will be on the remaining three variables.

400 microliters of saturated NaCl solution were taken into a syringe, then the syringe was put on the pump and the flow rate was set to 10 μL/min. A high voltage ranging from 0 kV to ±3 kV was applied to the syringe needle in increments of 1 kV. The nitrogen gas, with a pressure of 4 bar, was connected to a tee as a sheath gas. A square silicon wafer (1 x1 cm^2, smooth side up) was laid flatly on a platform as a substrate. The tip of the capillary tubing was positioned vertically at the center of the substrate, and the distance between them was set to 10 cm, 15 cm, and 20 cm. After a spraying time of 5 s, crystals or microdroplets were collected on the substrate. Experiments were conducted in a fume hood, and different ambient relative humidities (45%, 55%, and 65%) was controlled using a humidifier and a dehumidifier. The temperature was maintained at room

temperature, 20 ℃.

Preparation of KCl crystals

The preparation of KCl crystals is essentially identical to that of NaCl crystals. To illustrate that this charged microdroplet method is not limited to NaCl, we presented the hollow KCl single crystals obtained under conditions of a relative humidity of 55%, a height of 15 cm, and a voltage of +1 kV, as shown in Fig. S21.

Characterizations

The morphologies were characterized by optical microscopy (Leica, DM2700M), scanning electron microscopy (SEM, Zeiss, GeminiSEM 500), and transmission electron microscopy (TEM, Thermo Fisher, FEI Talos F200X). SEM imaging was performed at an accelerating voltage of the range of +1 kV to +3 kV, and secondary electron images were captured for suface morphology analysis. The element analysis was characterized by energy dispersive X-ray spectroscopy element mapping (EDS, Oxford Instruments, Ultim Extreme). The substrate for TEM was a carbon support film on copper grid (300 mesh). TEM analysis was conducted at an acceleration voltage of 200 kV, capturing transmission electron images for detailed internal structure examination. Selected Area Electron Diffraction (SAED) patterns were acquired to determine the crystallographic orientation and phase information of the analyzed regions. Particle size distribution (PSD) was statistically analyzed using the software image J.

2. Supplementary figures
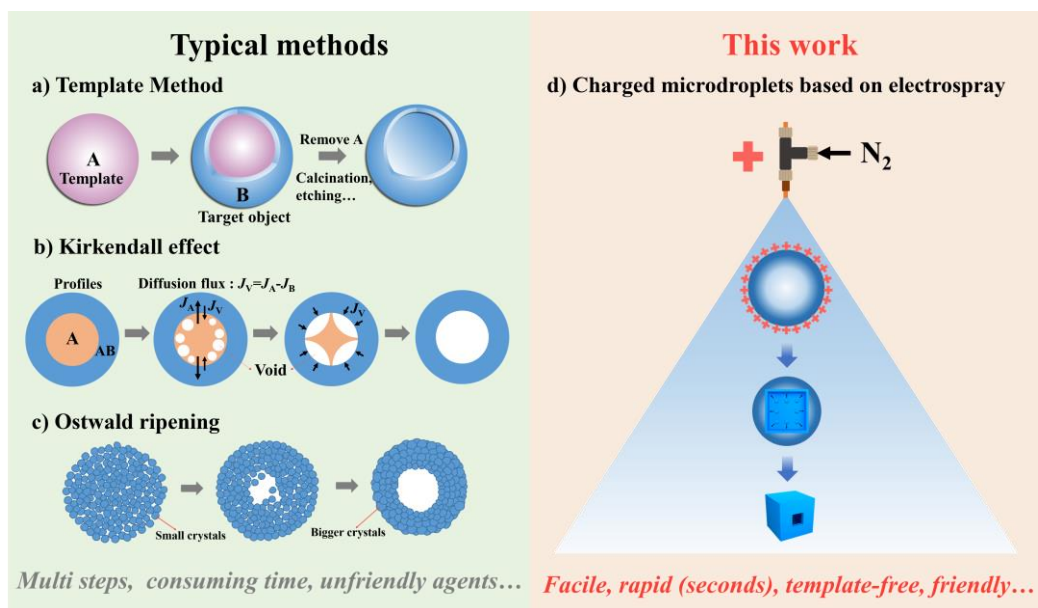
Fig. S1 Schematic diagram of methods for preparing hollow structures. (a) Template method is that target object grows on the template consisting of hard templates and soft templates which is eliminated by calcination or etching afterwards.[1] (b) Kirkendall effect occurs and slowly produces inner space owing to atomic vibrations deviating from their equilibrium positions and a discrepancy on diffusion rate between two or more components.[2] (c) Ostwald ripening is a phenomenon small crystals or particles dissolve and then deposit on larger ones and gradually form empty inside.[3] (d) Charged microdroplets method based on electrospray.
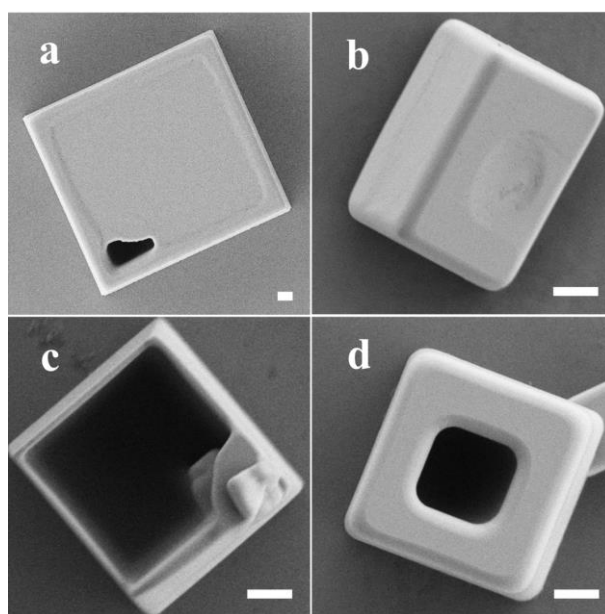
Fig. S2 SEM images of hollow NaCl crystals. Scale bar: 1 μm.
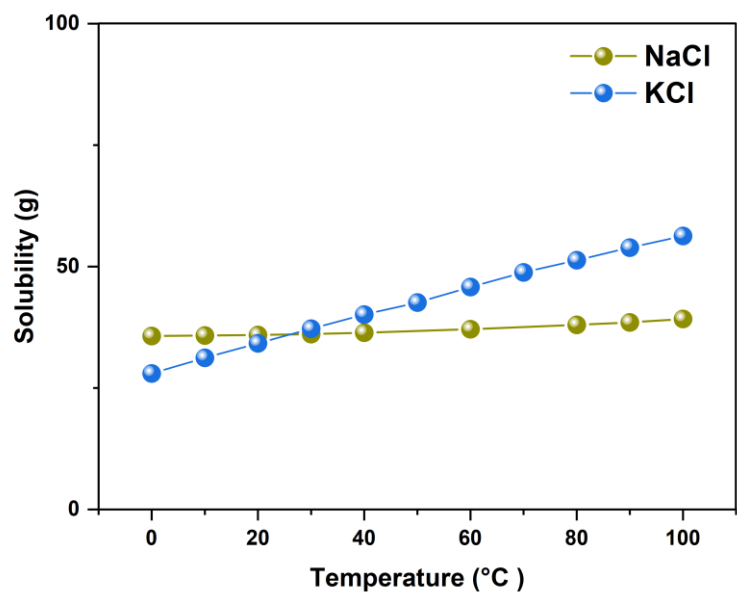
Fig. S3 Solubility of NaCl and KCl in water variation with temperature. [4]
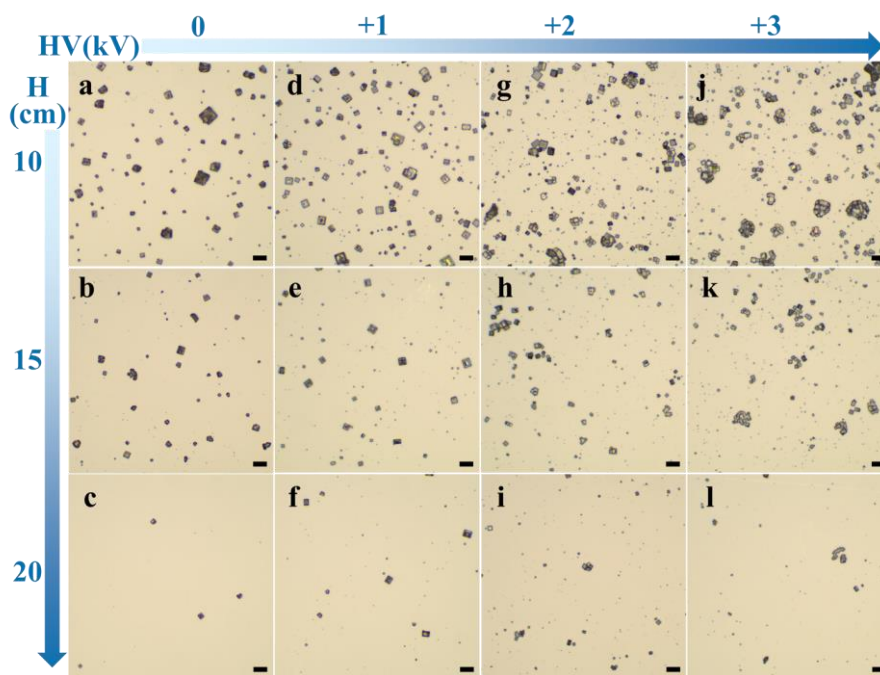
Fig. S4 Optical images of NaCl crystals at a relative humidity of 45% at different heights and positive voltages. Scale bar, 20 μm.
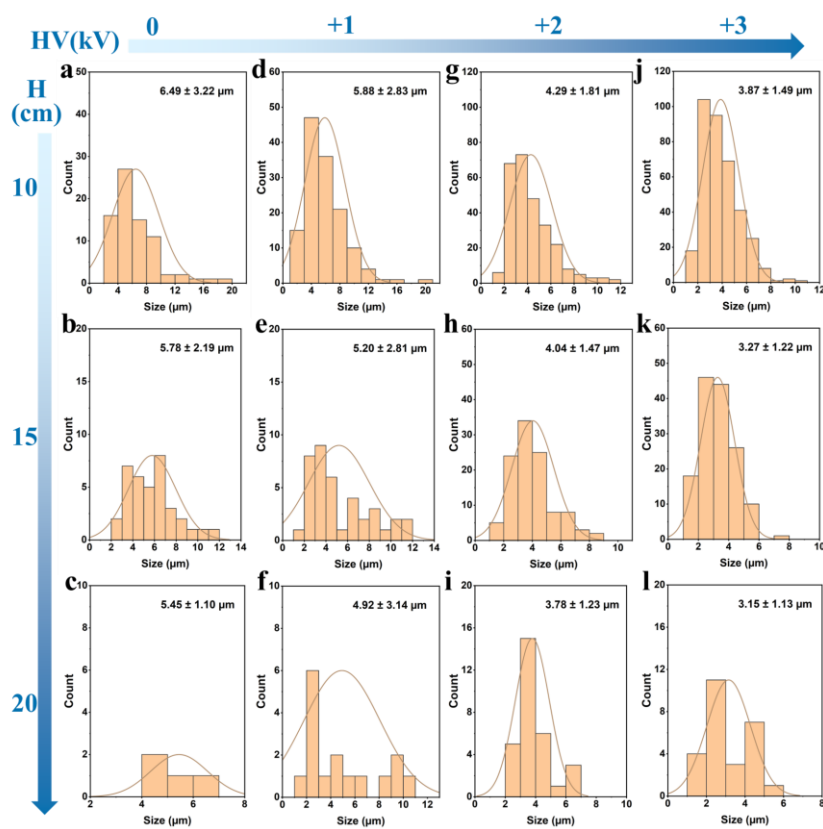
Fig. S5 Particle size distribution histogram of NaCl crystals at a relative humidity of 45% at different heights and positive voltages according to Fig. S4.
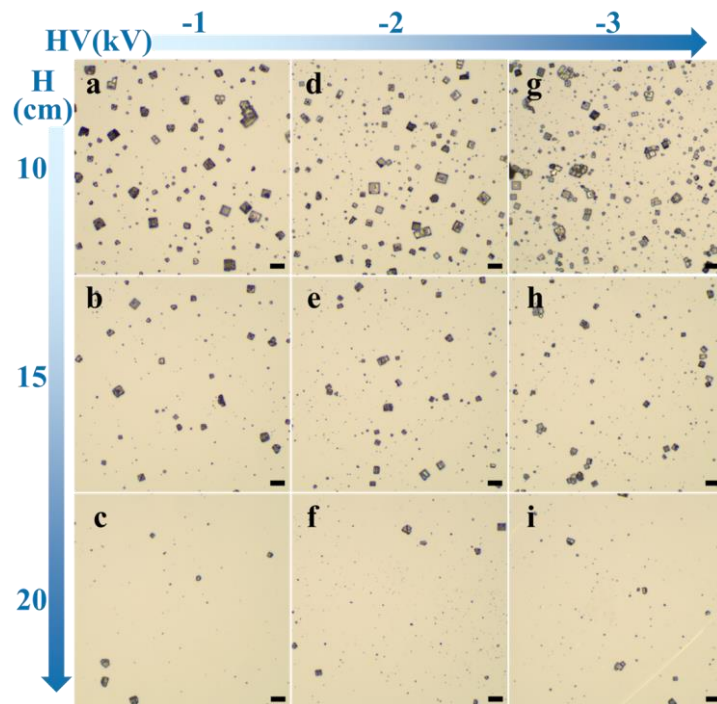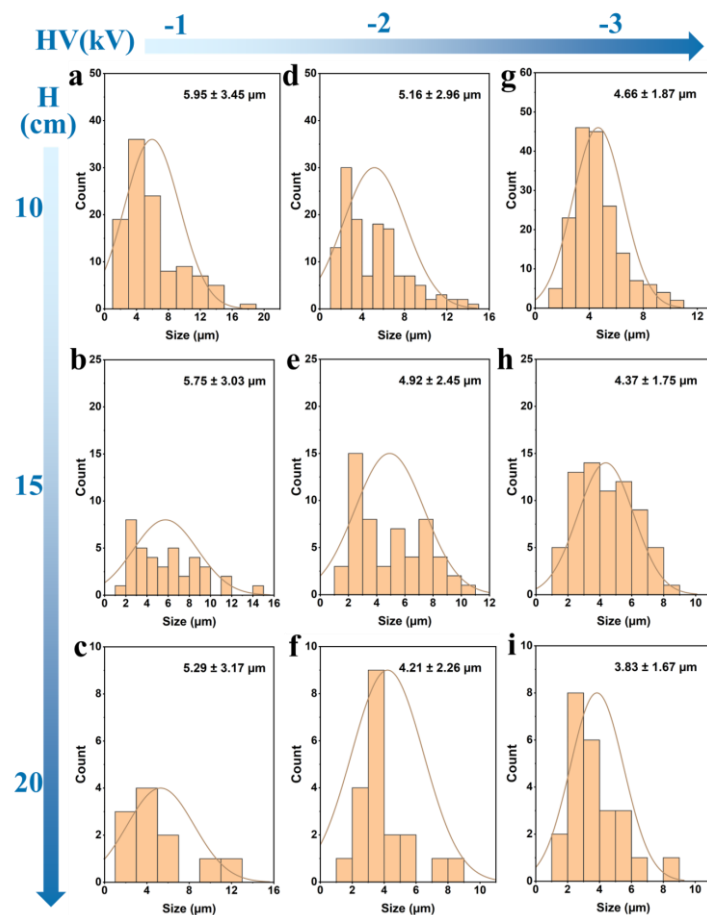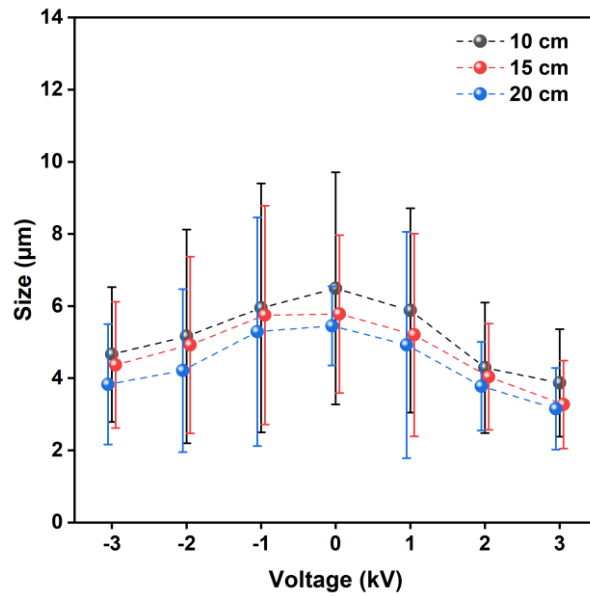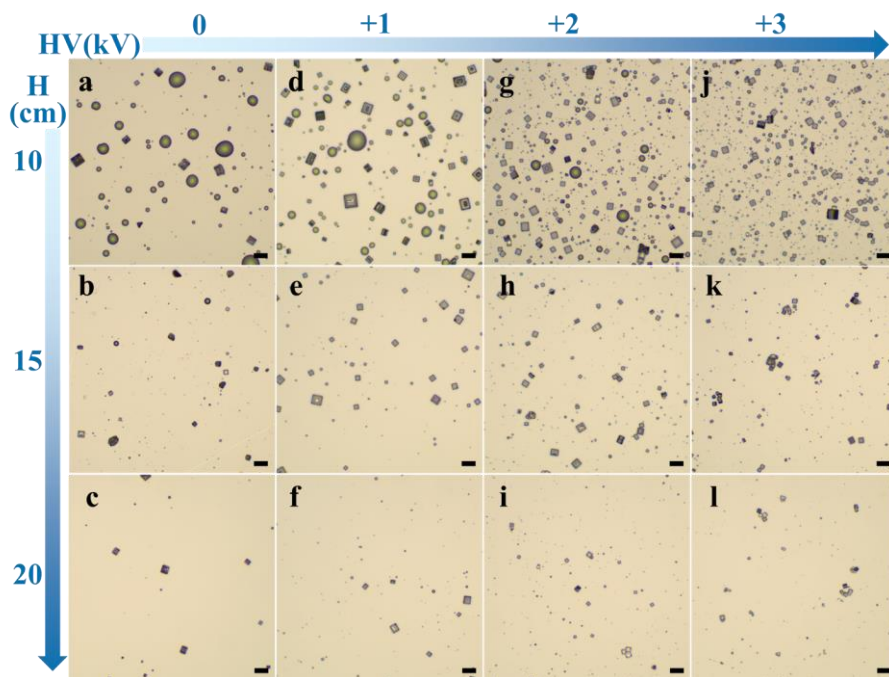
Fig. S6　Optical images of NaCl crystals at a relative humidity of 45% at different heights and negative voltages. Scale bar, 20 μm.

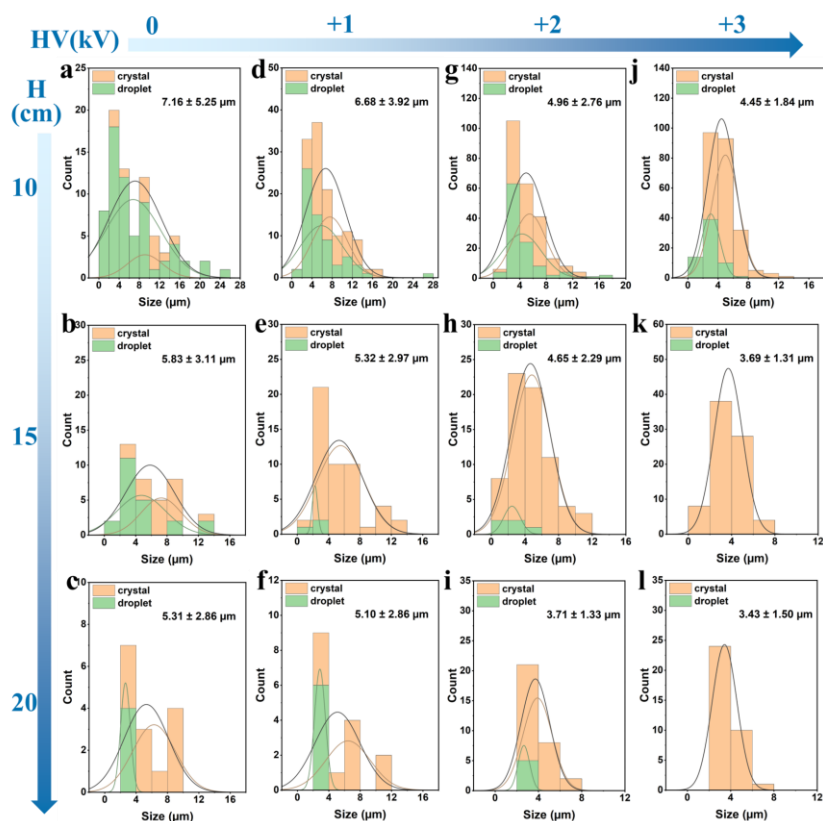**Fig. S7**　Particle size distribution histogram of NaCl crystals at a relative humidity of 45% at different heights and negative voltages according to Fig. S6.

Fig. S8 Mean particle size and standard deviation of NaCl crystals at a relative humidity of 45% at different heights and positive voltages.
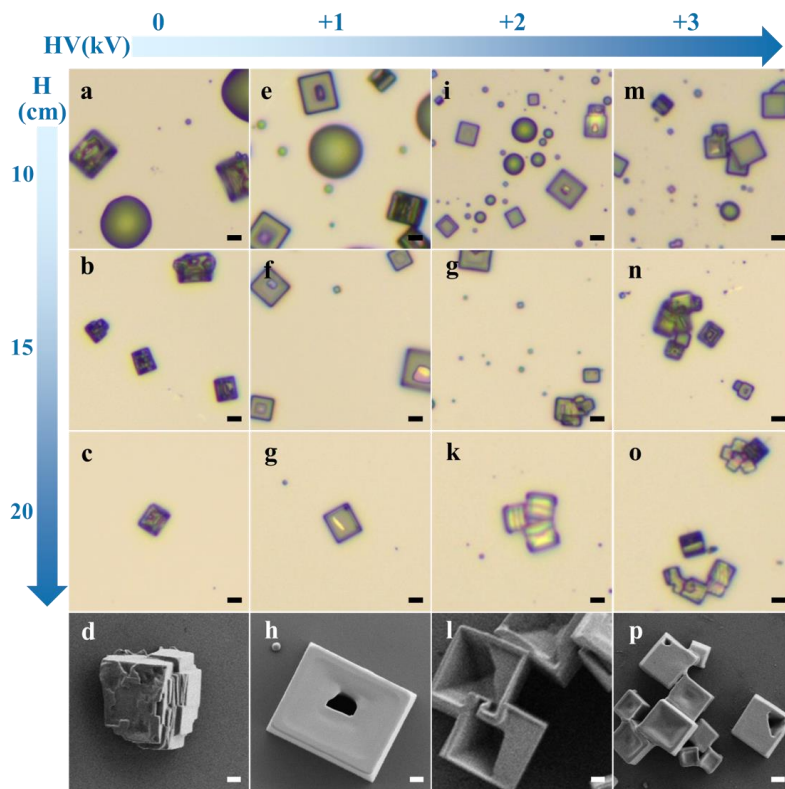
Fig. S9 Morphology images of NaCl crystals at a relative humidity of 55% at different heights and positive voltages. Optical images of (a-c, e-g, i-k, m-o, scale bar, 5 μm). Representative SEM images corresponding to different voltages of (d, h, l, p, scale bar, 2 μm).

Fig. S10 Optical images of NaCl crystals at a relative humidity of 55% at different heights and positive voltages. Scale bar, 20 μm.

Fig. S11 Particle size distribution histogram of NaCl crystals and droplets at a relative humidity of 55% at different heights and positive voltages according to Fig. S10.
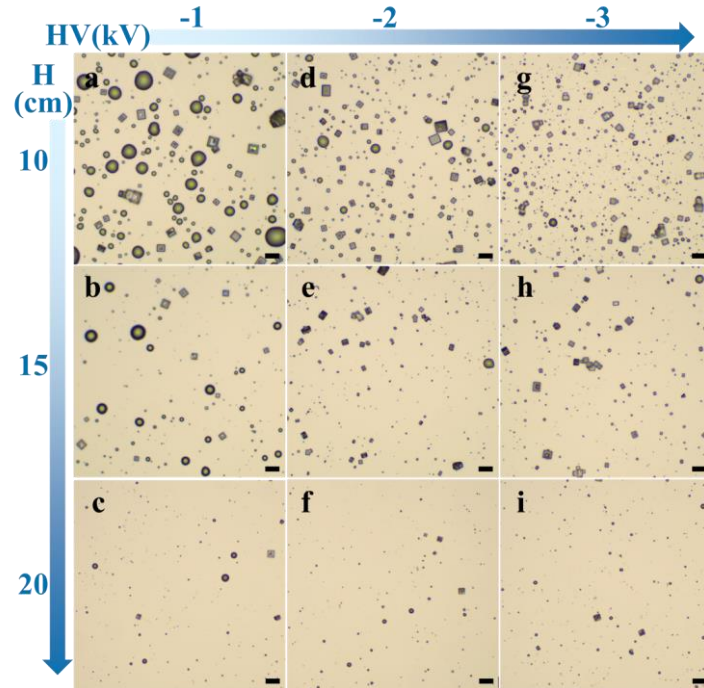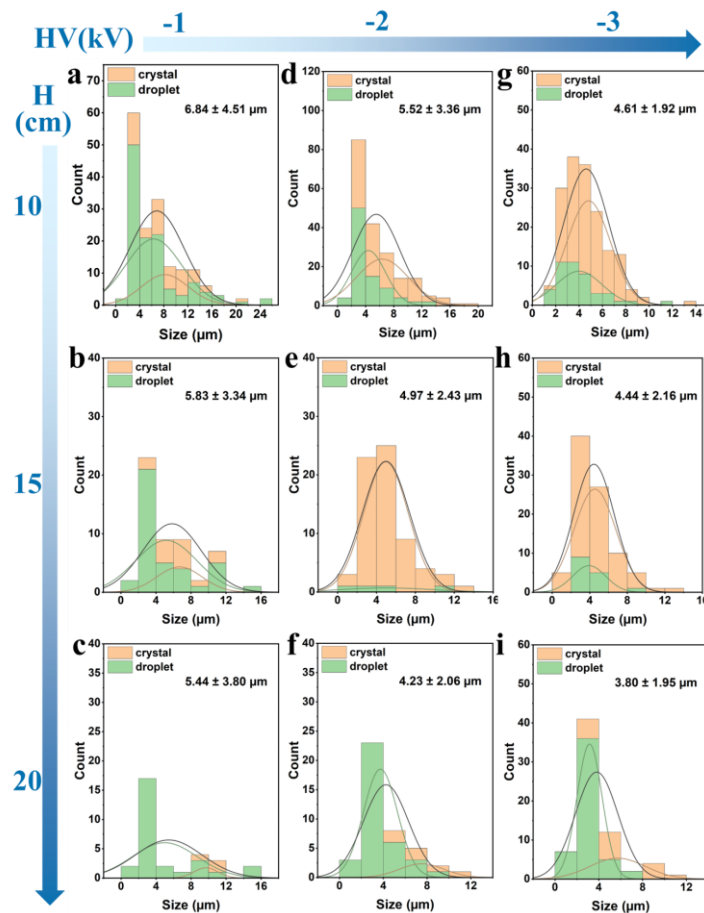
Fig. S12. Optical images of NaCl crystals and droplets at a relative humidity of 55% at different heights and negative voltages. Scale bar, 20 μm.

Fig. S13 Particle size distribution histogram of NaCl crystals and droplets at a relative humidity of 55% at different heights and negative voltages according to Fig. S12.
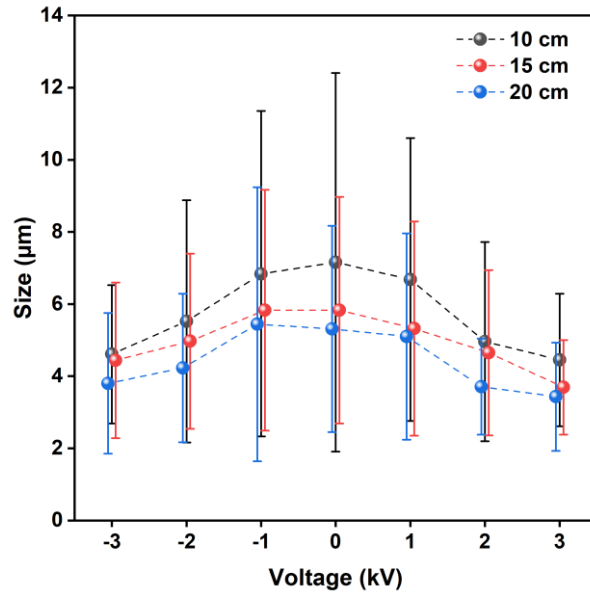
Fig. S14. Mean particle size and standard deviation of NaCl crystals and droplets at a relative humidity of 55% at different heights and voltages.
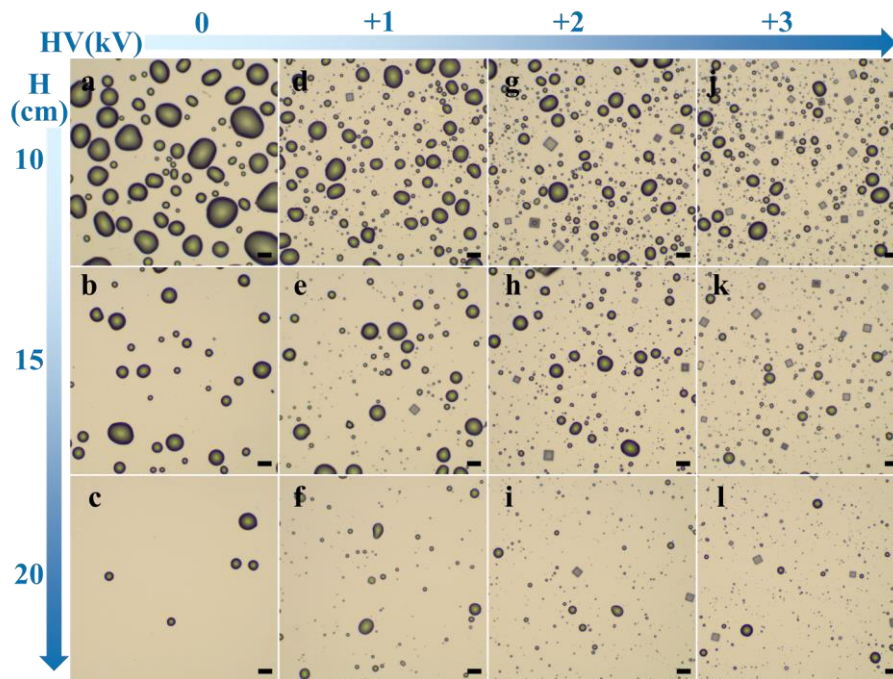
Fig. S15 Optical images of NaCl crystals at a relative humidity of 65% at different heights and positive voltages. Scale bar, 20 μm.
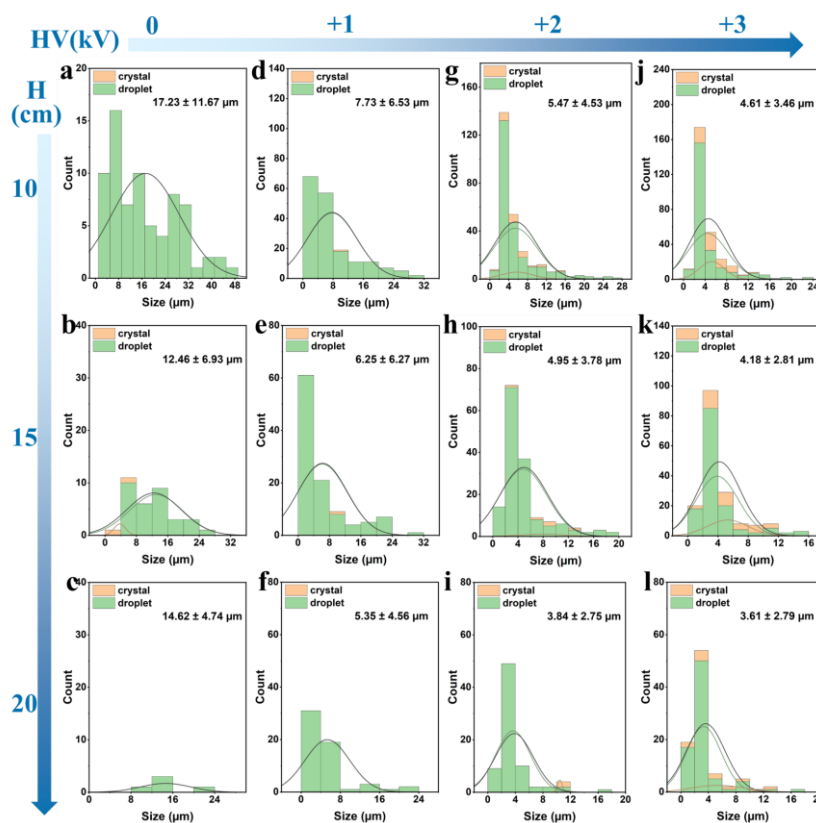

Fig. S16 Particle size distribution histogram of NaCl crystals and droplets at a relative humidity of 65% at different heights and positive voltages according to Fig. S15.
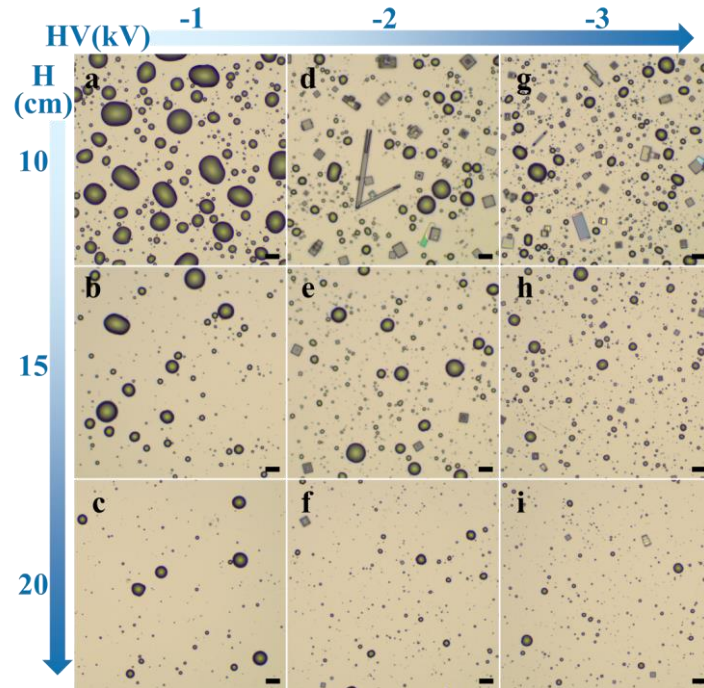
Fig. S17 Optical images of NaCl crystals at a relative humidity of 65% at different heights and negative voltages. Scale bar, 20 μm.
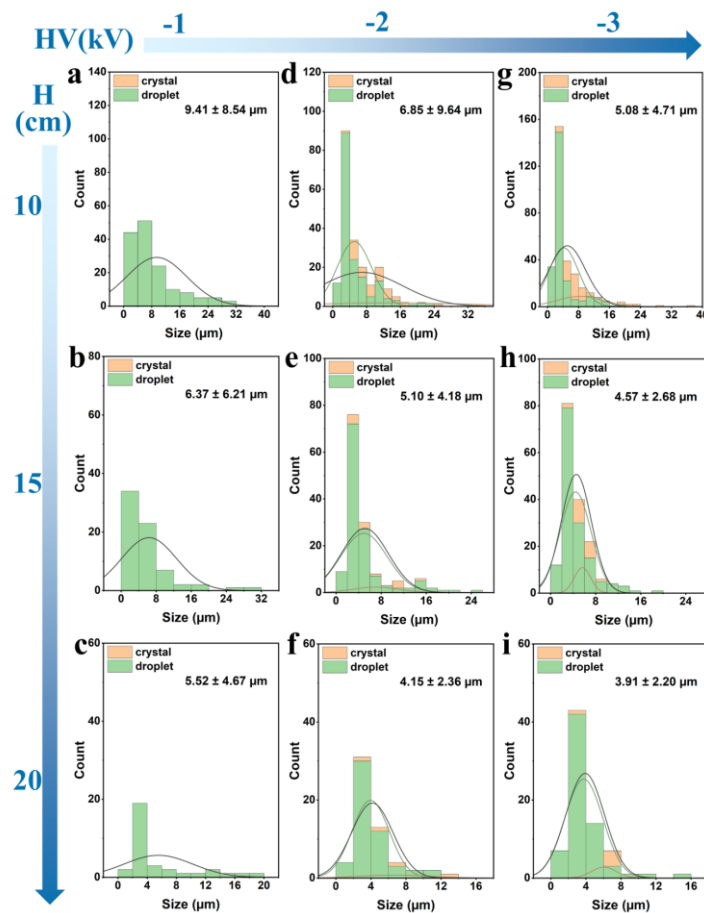

Fig. S18 Particle size distribution histogram of NaCl crystals and droplets at a relative humidity of 65% at different heights and negative voltages according to Fig. S17.
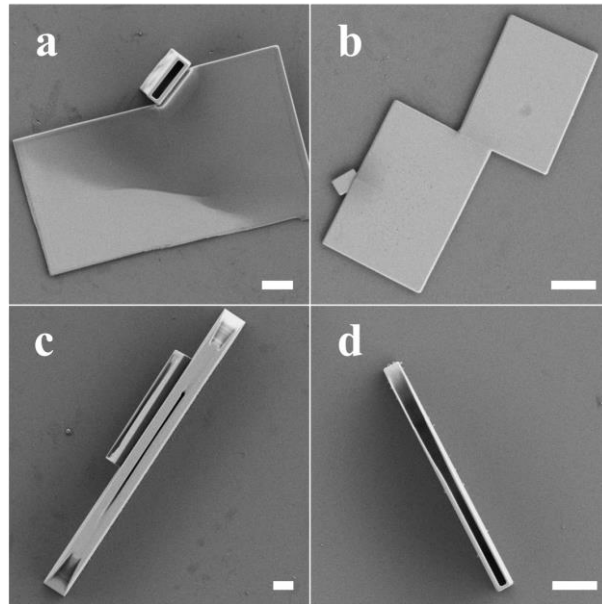
Fig. S19 SEM images of NaCl crystals. (a, b) flake. (c, d) stick. Scale bar, 4 μm. Flake crystals, as we define them, adopt a large, flat-tiled configuration, and the bending observed in the images indicates their thin and typically lamellar nature. Stick crystals, as we define them, exhibit very small surface areas with a high aspect ratio.
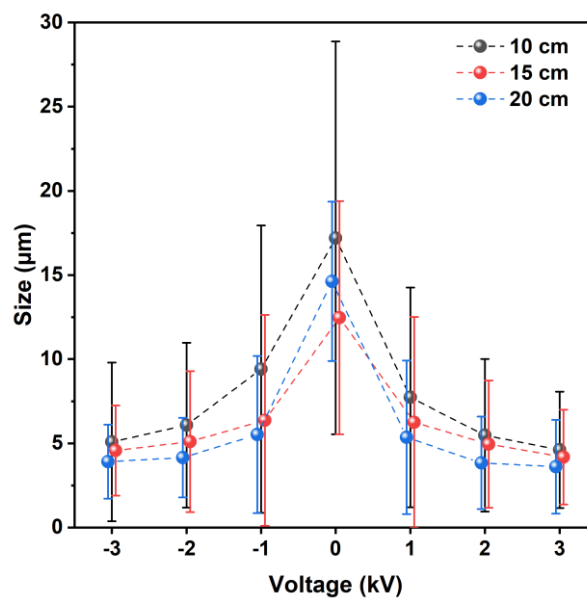

Fig. S20 Mean particle size and standard deviation of NaCl crystals and droplets at a relative humidity of 65% at different heights and voltages.
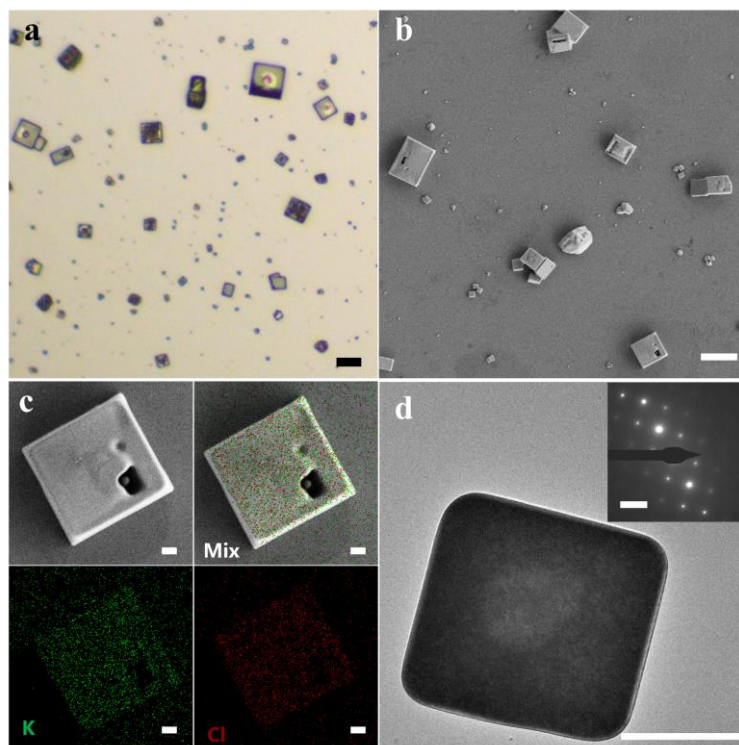
Fig. S21 Morphology images of KCl crystals at a relative humidity of 55% at a height of 15 cm and a voltage of +1 kV. (a) Optical image. (b) SEM image. (c) EDS elemental mappings. (d) TEM image. Inset: SAED pattern. Scale bar: (a, b) 10 μm; (c) 1 μm; (d) 1 μm, inset: 5 nm^{-1}.

3. References

1. F. Caruso, R. A. Caruso and H. Mohwald, *Science*, 1998, **282**, 1111-1114.
2. H. J. Fan, U. Gosele and M. Zacharias, *Small*, 2007, **3**, 1660-1671.
3. H. Chun Zeng, *Current Nanoscience*, 2007, **3**, 177-181.
4. G. S. James, *CD & W Inc, Wyoming*, 2005.