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Capillary-assisted localized crystallization on discrete micropillar rings

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Microcrystals with defined sizes, morphologies, and locations provide a core opportunity for applications in microelectronic devices and microoptical components. Herein, a simple method was developed to obtain microcrystals with controlled sizes and locations by capillary-assisted localized crystallization, which utilizes “discrete micropillar rings” (DMRs) to mediate the solution evaporation process. Being different from conventional hydrophilic/hydrophobic modified surfaces, DMRs can guide the movement of three-phase contact lines, confine the solution residing inside the rings with a high concentration ratio, and help to crystallize microparticles (NaCl or CaCO3) without any further surface modification. Microcrystal sizes can be tuned in a wide range (from the order of ~μm2 to that of ~100 μm2) by changing the geometric parameters (height, pillar interval, and diameter) of pillar arrays. This facile, scalable, and low-cost technique for generating microcrystals with controlled size and location inside the DMRs holds great promise for micro-electronic and micro-optoelectronic applications. Published by AIP Publishing. https://doi.org/10.1063/1.5063608

Crystal nucleation and growth at microscale has long been attracting researchers’ interest due to its significant importance in physical systems and chemical processes.1,2 Deterministic control of crystal particle size, shape, and growth position is a critical mission for the development of functional microdevices, including microelectronics, micro-optoelectronics, and microsensors.3,4 For example, controllable crystallization of rubrene can facilitate high-performance organic field-effect transistors (FETs) in flexible and printable microelectronics.5 Miniaturized optical lens arrays can be obtained by controllably crystallization of organic or inorganic components for super-resolution nano-imaging and bio-sensing. To achieve designable crystallization of organic or inorganic compositions, a variety of approaches have been explored to mediate the crystallization process and control the crystal size and morphologies such as the usage of soluble additives.8 Besides, microfluidic devices with pillar-structured silicon substrates have been fabricated to generate microcrystals by providing a confined reaction volume.9 In addition, superhydrophobic silicon pillars with high adhesion have been employed to yield patterned microcrystal arrays on top of the micropillars.10,11 However, these microfluidic or superhydrophobic microstructures need a tedious and time-consuming production process involving lithography, transfer, etching, or surface modification. And the type and the dimension of as-prepared structures are rigidly limited by the photomasks. Moreover, sophisticated manipulation of fluids or liquid droplets is commonly needed,9,10 e.g., clinging microdroplets upon microstructures or rapidly scanning a droplet over the micropillars.10,11

Here, we present a facile strategy for generating controllable microcrystals with the aid of “discrete micropillar rings” (DMRs). The microcrystals are directly formed on the DMR surface by capillary-assisted localized crystallization. During solvent evaporation, the DMRs form a localized microenvironment and guide the movement of three-phase contact line (TCL), resulting in the confined solution residing inside the DMRs with a high concentration ratio at the final stage. The size of microcrystals can be deliberately controlled in a wide range by changing the DMR geometric parameters and the concentration of the crystallization mother liquid. The effect of DMR parameters including the height, the pillar interval, and the diameter on the size of microcrystals is systematically studied.

The experimental process is illustrated in Fig. 1, which can be mainly divided into two stages. The first is the fabrication of DMRs on a glass substrate by femtosecond laser direct writing and subsequent development (details can be found in supplementary material, Sec. 1). Femtosecond laser direct writing has high flexibility and micropillar arrays with various geometries can be readily created.12–14 Self-organization of nanofibres and nanomembranes has been explored by femtosecond laser writing, which is achieved only in the organic photocurable resins.15,16 Therefore, microstructure induced microcrystallization of different materials is still in high demand. Next, the DMRs are immersed in the mixture of an aqueous solution of sodium chloride (NaCl) and ethanol for around 5 minutes. Here, ethanol is used as an auxiliary material to increase the structure surface wettability due to its relatively lower surface tension (the detailed influence of ethanol on the liquid-polymer wetting properties is discussed in supplementary material, Sec. 2 and Fig. S1). NaCl is chosen for proof-of-concept demonstration first because of its importance.
in many natural and industrial processes and second due to its rich polymorhism.\textsuperscript{17} NaCl has different crystalline structures as determined by precipitation pathways, and is usually in an anhydrous form at room temperature.\textsuperscript{18}

After being taken out from the mother solution, the sample is placed in an ambient environment for drying. It is found that microscale crystals were generated inside the closed ring region surrounded by micropillars after the liquid dried completely. The dynamics of microcrystal formation is attributed to the effect of DMRs on TCL movement. Along with the solvent evaporation, the amount of liquid became less gradually and the TCL moved. When the TCL touches the DMRs, the movement of TCL is guided by DMRs, resulting in the phenomenon that the liquid is confined inside the DMRs in the end. At this stage, the solution is saturated or supersaturated due to evaporation of solvent, making it easy to crystallize microparticles. Scanning electron microscopy (SEM) images show that the microcrystals stay only inside the micropillar array and the peripheral area remains clean. In comparison, evaporation and crystallization of NaCl solution on a flat surface without micropillars is studied and shown in supplementary material, Sec. 3 and Fig. S7. The dynamic process of crystallization on the pillar-structured surface can be experimentally verified by in-situ observation using an optical microscope. A series of video captures [Fig. 1(b) and supplementary material, video S2] clearly show the movement of TCL during the liquid evaporation. With the aid of micropillars governing the TCL movement derived from capillary forces, the solution spontaneously contracted into the confined liquid region surrounded by micropillars, yielding microscale crystals inside the pillars arrays.

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The geometry of the DMRs can appreciably influence the crystallization. Figures 2(a)–2(d) show the top view SEM images of the microcrystals formed in the DMRs with four different pillar heights. It can be seen that the size of crystals shows good consistency in the DMRs with the same height, revealing fine controllability of the DMR-dominant particle preparation. Here, for convenience, we define the crystal particle size as the area occupied by the microcrystal. Four kinds of DMRs with different heights of 1 \( \mu m \), 3 \( \mu m \), 5 \( \mu m \), and 7 \( \mu m \) and the same diameter of 10 \( \mu m \) are investigated, respectively. The concentrations of the aqueous salt solution is 0.5 M and ethanol is added with a volume ratio of 1:1. The detailed size information of microcrystals in each array can be seen in Figs. 2(e) and 2(f), showing that the sizes of the microcrystals increase with the height of micropillars. That is because the height of TCL-confined liquid droplets is...
determined by the height of the pillar. In this way, more liquid remains in the ring region surrounded by higher pillars than lower pillars. When the pillar height is further increased to more than 10 μm, the pillared rings can be assembled into flower-like structures due to the large capillary force \(^{18}\) (supplementary material, Fig. S8). However, microcrystals can still be generated inside the assemblies. In brief, the microcrystal size can be finely tuned by varying the pillar height.

Besides the pillar height, the influence of the pillar interval and the ring diameter on the average size of microcrystals is investigated. In order to vary the interval between micropillars, while keeping the ring diameter constant, we constructed DMRs with different numbers of micropillars. Figures 3(a)–3(c) show the SEM images of microcrystals generated in the DMRs with different geometrical parameters. The sizes of microcrystals in DMRs with a larger interval are much smaller than those of DMRs with a smaller interval. The volume of liquid restricted by DMRs with a larger interval is less than that by DMRs with a smaller interval because of the longer meniscus interface between neighboring pillars. It is found that nothing is formed in the DMRs with an interval of 3.5 μm or larger (supplementary material, Fig. S9) due to the poor confinement ability of the sparse pillars. In other words, when the pillar interval is larger than 3.5 μm, no controlled microcrystals can be generated in the DMRs and the surface is similar to the flat surface, where random crystals may be generated on the whole substrate.

It is also found that the size of crystallized microparticles increases with the diameters of DMRs. This can be attributed to the increment of the confined solution volume as the ring diameter increases. Figures 3(d)–3(f) show the average statistics of the microcrystal sizes formed inside 5 μm-height DMRs with different diameters (10, 15, 20, and 25 μm) and different intervals (3.5, 2.5, and 1.5 μm). With the diameter of 25 μm, multiple crystals are formed in the DMRs and the size of the crystals particles can reach as large as 118 μm². The formation of multiple crystals is ascribed to the higher nucleation rate and more possible nucleation spots (NSs). As shown on the right of Fig. 3(b), two or more independent NSs can be formed during the solution evaporation inside the DMRs with the diameter of 25 μm and a pillar interval of 2.5 μm.

The concentrations of crystallization mother liquids can also tune the size of microcrystals. Two different concentrations (0.5 M and 5 M) of aqueous NaCl solution on the DMR surface with the same geometry are investigated. Three kinds of DMRs with different diameters (10, 15, and 20 μm) are employed to generate crystals. The detailed geometries of these microcrystals can be found in Figs. 4(a) and 4(b). The microcrystals generated from the low-concentration mother liquid are smaller compared with those from high-concentration mother liquid. Figure 4(c) shows the statistic values of crystal sizes generated from different crystallization mother liquids. The crystal grain size formed from 5 M NaCl solution...
A variety of closed micropillar array arrangements (triangle, second laser direct writing technique, the micropillars can be ized crystallization. Benefiting from the flexibility of femto-
the generation of microcrystals via capillary-assisted loca-
ners and dominates the crystallization process. The proposed
crystals in micropillar arrays of different shapes. All scale bars: 10 \mu m.

increases by approximately 1.5 times compared with that from 0.5 M solution.

Figures 4(d) and 4(e) show the generation of an array of microcrystals with a T-shape distribution (more shapes of microcrystal array can be seen in supplementary material, Fig. S10). An energy dispersive spectrometer (EDS) analysis is performed to verify that the NaCl microcrystals are formed as we designed by monitoring the chlorine element distribution. To further demonstrate the versatility of our method, other materials such as calcium carbonate (CaCO_3) are uti-

See supplementary material for the influence of ethanol on the liquid-polymer wetting properties, a comparison of evaporation and crystallization of NaCl solution on a flat surface, details about uniform closed rings and DMRs, a detailed discussion of the dynamics of TCL movements and crystal formation, and the diverse paradigm of microcrystal array generation.

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