Crystals of Crystals: Fabrication of Encapsulated and Ordered Two-Dimensional Arrays of Microcrystals

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This paper demonstrates a method of making ordered arrays of encapsulated microcrystals: "crystals of crystals". Single crystals may have properties useful for optical, magnetic and electronic applications.[1−3] Large single crystals can be difficult to grow; smaller single crystals can be easier to grow, but typically are heterogeneous in size and orientation.[4] The procedure described here generates arrays of small crystals (tenths to tens of micrometers) with control over their size, orientation, and arrangement in space. Previously, we and others have used patterned self-assembled monolayers (SAMs)[5−11] and microwells[12] to prepare arrays of microcrystals with limited control over their spatial arrangement.

In this work, we fabricated two-dimensional (2D) arrays of microcrystals of five inorganic (KBr, KH_2PO_4, NaCl, KNO_3, and $NaNO_3$) and two organic (hydroquinone and glycine) compounds (Figures 1−3) and characterized them by optical microscopy and powder X-ray diffraction (Figure 4). We begin with the fabrication of 2D arrays of microwells in the surface of poly(dimethylsiloxane) (PDMS) using soft lithography (Figure 1).[13] These wells are asymmetric, both to force crystallization to occur at a specific point in the well, and to direct the orientation of the crystal. We fill the wells using discontinuous dewetting.[14] As the array of microwells is pulled from the solution of material to be crystallized, solvent evaporates and crystallization or precipitation ensues.[15] The location of this initial crystallization or precipitation within a microwell is influenced by the orientation of the asymmetrical wells relative to the liquid−vapor interface and the gravitational vector. When precipitation ensued, the material is recrystallized by exposing the array of wells to vapors of the solvent (Figure 2).

As with other crystallizations, the conditions used to generate arrays of crystals depended on the compound and were developed experimentally. In general, the best results were obtained when the crystallization solution was kept at 45−50 °C. In some cases (e.g., glycine, Figure 3) solvent remained adsorbed on the precipitates when the patterned PDMS was withdrawn from the solution. In such cases, the adsorbed solvent was removed by heating the substrate on a hot plate prior to the recrystallization. We have attempted the crystallization of a number of compounds, and Figures 1−3 illustrate some successful examples.

In two examples, we have used microwells as microreactors: that is, as microvessels in which to carry out chemical reactions in specific locations on a surface with picoliter volumes of chemicals. The crystals of KNO_3 and $NaNO_3$ shown in Figure 3 were obtained by exposing the precipitates of KOH and NaOH to the vapors of fuming HNO_3 for ∼5 min. Formation of product (KNO_3 and $NaNO_3$) crystals was confirmed by X-ray diffraction (Figure 4). We collected the X-ray data in $\theta - \theta$ scan mode. In this mode, only diffracting planes parallel to the surface of the substrate produce

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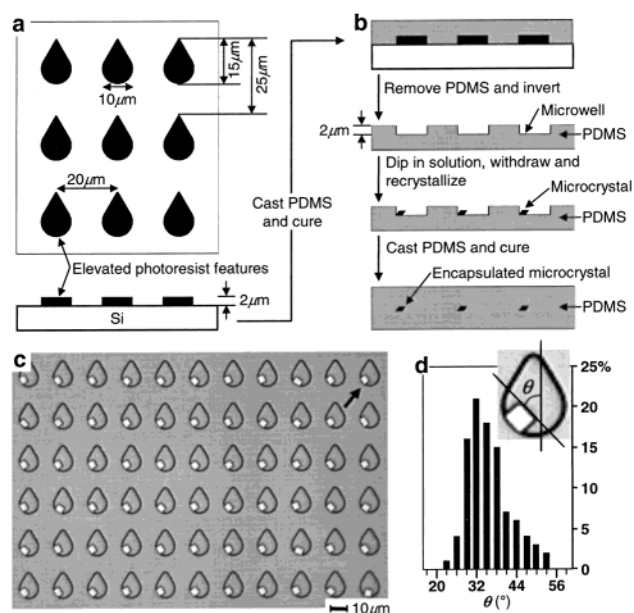
Figure 1. Experimental design for crystallization and encapsulation in microwells. (a) Patterned photoresist features fabricated on Si-wafer using photolithography. (b) Schematic representation of the process; dimensions not to scale. (c) Optical micrograph of ordered arrays of KBr microcrystals with a density of 2×10^5 crystals cm^{-2}. These crystals nucleate from (200) planes; they are not encapsulated. The arrow in this and the following figures indicates the direction in which the substrate is withdrawn from the solution. (d) Histogram showing the distribution of orientations of KBr microcrystals. 40% of the crystals lie within 3° and 70% within 9° of a mean θ value (33.5°); 3% of the crystals lie outside the region shown.
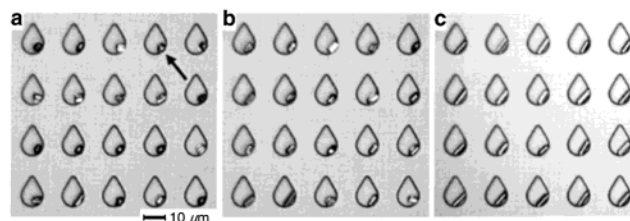

Figure 2. Recrystallization of KH_2PO_4 in arrays of microwells. Precipitated KH_2PO_4 is exposed to water vapor in cycles of 2 s. Snapshots taken after first (a), fifth (b), and tenth (c) cycle illustrate the progression of recrystallization. The 10-μm scale bar applies to all images.

significant diffraction intensity. In all examples described here, the crystals nucleated specifically from one or two crystallographic planes. We have not established the mechanism(s) responsible for this selection.

We analyzed the angular spread or distribution of orientations of microcrystals within the plane of the substrate by measuring the
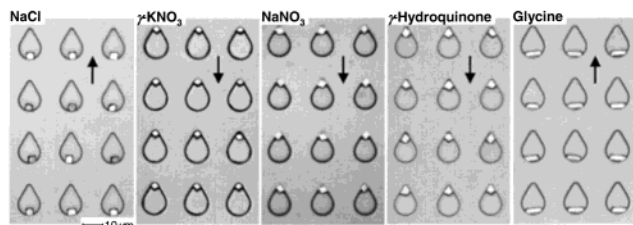
Figure 3. Ordered arrays of microcrystals. The site of crystallization within the microwells depends on the pulling directions. The 10-μm scale bar applies to all images.
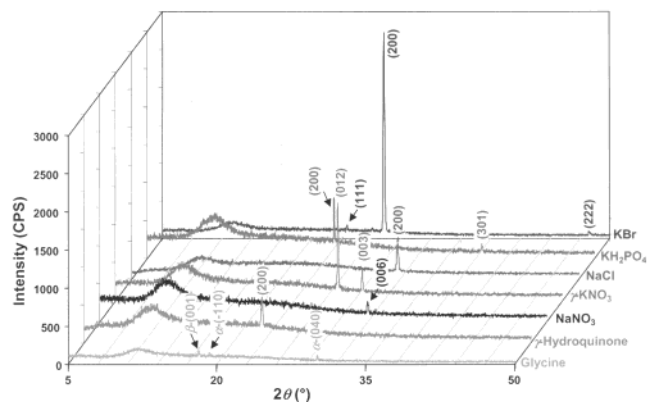

Figure 4. X-ray diffraction data of ordered arrays of microcrystals. The indices of crystallographic planes are indicated over the corresponding diffraction lines. The broad peak at ∼12° indicates the diffraction from the PDMS substrate.
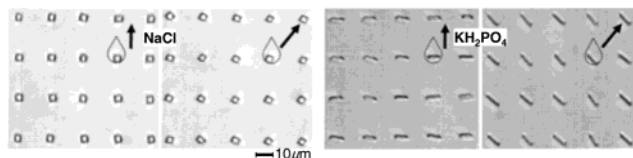

Figure 5. Ordered arrays of microcrystals encapsulated in PDMS. The crystallization is steered to predetermined locations in microwells to control the mutual orientations of crystals. A microwell is drawn on each image to show the location of crystals prior to encapsulation. (Left) Microcrystals of NaCl formed in two different mutual orientations. These crystals nucleate from (200) planes. (Right) Microcrystals of KH_2PO_4 formed in two different mutual orientations. These crystals nucleate from (200) planes; the long axes are parallel to c-axis. The 10-μm scale bar applies to all images.

values of θ (angle between an edge of the crystal and vertical; see Figure 1d, inset) for 200 randomly selected KBr microcrystals. Figure 1d is a histogram showing the fraction of crystals falling within the ranges of θ; this histogram indicates a narrow distribution of orientations of KBr microcrystals. Other arrays of microcrystals exhibited similar distributions of orientations.

Figure 5 shows the influence of the angle at which a PDMS substrate was withdrawn from the solution (and thus the direction of "down" in the gravitational field) on the orientations of NaCl and KH_2PO_4 microcrystals. Figure 5 also shows the protection of arrays of microcrystals embedded in a matrix of PDMS.[16] The protected arrays of microcrystals remained stable for more than 6 months and retained their orientation. Figure 6 shows that we can control the size of microcrystals by controlling the concentration of the solution. We made uniform arrays of submicrometer-sized crystals with lateral dimensions as small as 400 nm.
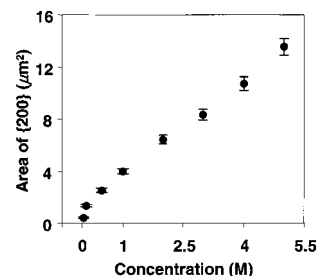

Figure 6. Dependence of size of NaCl microcrystals on the concentration of solution. NaCl crystals nucleate from (200) planes; the size of the crystals is estimated as the surface area of exposed {200} faces. At each concentration, the surface area is measured for 40 randomly selected crystals.

Using a compound that forms crystals readily, this method consistently produces one crystal per well, forms ordered arrays of uniformly sized microcrystals, confines the crystals to specific locations within the wells, controls relative orientations of crystals within an array to produce a 2D "crystal" of microcrystals, and encapsulates these crystals in a transparent elastomeric polymer, both to protect them and to allow them to be manipulated. Crystallization in microwells demonstrated in this paper is different from the crystallization on patterned SAMs (studied previously) in its ability to orient the crystals that form.

This methodology makes it possible to fabricate ordered arrays of statistically significant numbers of uniformly sized microcrystals, with control over their spatial orientation. We believe that this technique has the potential to be useful in studying fundamental aspects of nucleation and crystal growth, and in forming arrays of microcrystals for use in optical and magnetic data storage and communication.[17]

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