

Thermally Induced Unidirectional Crystallization of Charged Colloids

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荷電コロイド粒子分散液は、粒子間の静電相互作用が十分大きいとき、粒子が規則配列した“結晶”構造を形成する。本研究では、昇温により粒子表面電荷数が増加して結晶化するコロイド系(ピリジン共存シリカ粒子/水分散液; 粒径 ~ 100 nm; 粒子体積分率 = 0.035)を用い、加熱により結晶を一方向成長させた。大型(1 mm \times 1 cm \times 3 cm)かつ試料セル壁面に良好に配列した、単一ドメイン結晶が生成した。結晶化機構および成長曲線について、試料温度分布の測定結果に基づいて議論する。

1. Introduction

Charged colloidal particles dispersed in water self-assemble into “crystal” structure, when the electrostatic interparticle interaction is sufficiently strong.¹ These colloidal crystals have received considerable attention as photonic crystals since their Bragg wavelengths usually lie in the visible light regime. Thus, ingenious crystallizations² have been developed to date.

In ordinary crystalline materials, large single-crystals are produced by unidirectional solidification under a temperature gradient (e.g., Bridgman method). Although temperature T is a weak parameter for colloidal interactions,¹ it induces the crystallization of colloids indirectly. It has been reported that hard-sphere colloids exhibit thermally driven crystallization due to a gradient in the particle volume fraction ϕ , which is generated by a gradient of T .³

For charged colloids, the gradients in electrostatic interaction magnitude induced by T should result in directed crystallization. An earlier study⁴ showed that a homogeneous silica colloid containing a weak-base pyridine (Py) crystallizes with increasing T and not solely by increasing Py concentration [Py]; this was attributed to an enhanced dissociation of Py ($\text{Py} + \text{H}_2\text{O} \leftrightarrow \text{PyH}^+ + \text{OH}^-$, where PyH^+ denotes pyridinium cation) at high T and/or a reduction in the permittivity of water with increasing T . The crystallization was thermoreversible, and the crystallization temperature T_C , which was tunable near the room temperature T_R , was higher at lower [Py].

Based on this, here, we report a novel directed crystallization of dilute colloidal silica in coexistence with Py, under a temperature gradient.⁵ This method enables the fabrication of well-oriented and large (1 \times 10 \times \sim 30 mm) single-domain crystals in a short time (<10 min). Moreover, the crystals have sharp and deep transmission dips as well as good spatial uniformity in the Bragg wavelength λ_B ($\sim 0.1\%$).

2. Materials and Methods

Aqueous colloidal silica (particle diameter = 110 nm; particle volume fraction $\phi = 0.035$) was purified as described elsewhere.^{2b} T_C value was controlled by changing [Py]; at [Py] = 27.5 and 35 μM , $T_C = 35$ and 19 $^\circ\text{C}$, respectively. Figure 1 illustrates the experimental setup. A colloid sample was introduced into a quartz cell (inner dimensions = 1 \times 10 \times 44 mm; wall thickness = 1 mm). The open end of the cell was sealed with plastic film, and the cell was placed horizontally to minimize the disturbance caused by convection on the crystal growth. Then, the other end of the cell was contacted with a copper heater block maintained at $T = T_0$. All the experiments were performed in a room thermostated at $T_R \sim 23$ $^\circ\text{C}$.

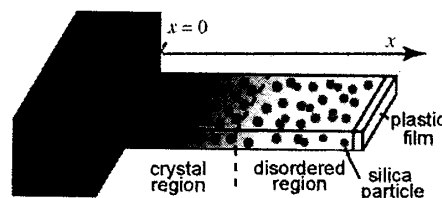


Figure 1. Experimental setup used for the thermally induced crystallization.

3. Results and discussion

We used a sample having $T_C = 19$ $^\circ\text{C}$ ($<T_R$) that had been cooled to 5 $^\circ\text{C}$ beforehand so that it took a disordered state; T_0 was 40 $^\circ\text{C}$. The disordered region had an opaque appearance, while the crystal region exhibited a uniform diffraction color. Within ten minutes the crystal length was a few centimeters. The cell was

then separated from the heater block and equilibrated at T_R . Since $T_C < T_R$, the crystal structure was maintained, which facilitated further examinations. The diffraction color of the crystal clearly exhibited an angular dependence, implying that the crystal was well oriented. Furthermore, the crystal had good transparency.

The optical property of the crystal was examined in greater detail by applying fiber optics transmission spectrometry at various locations x (Fig.1); the measurements were performed in circular areas with diameters of ~ 1 mm in a direction normal to the horizontal cell surface. Figure 2 depicts the spectra measured at $x = 0-30$ mm at 5-mm intervals. The spectrum before the crystallization is shown in Fig.2 by the dashed curve for comparison. Enlarged spectra around the dips are shown in Fig.2 (inset). The crystal had sharp and deep dips at $\lambda_B \sim 616$ nm despite having a thickness of 1 mm; the half-dip width was 5.8 nm on average, and the minimum transmittance reached nearly 0.005. These are comparable to the best results reported for thin crystals. Furthermore, the crystal showed good optical uniformity over the entire region. The variation of λ_B with x was 0.8 nm (0.1% of λ_B) in standard deviation. Laser diffraction experiments suggested that the present crystals had single-domain structures with normal or twin body-centered-cubic (b.c.c.) lattice symmetries, whose (110) plane were oriented parallel to the horizontal cell wall.

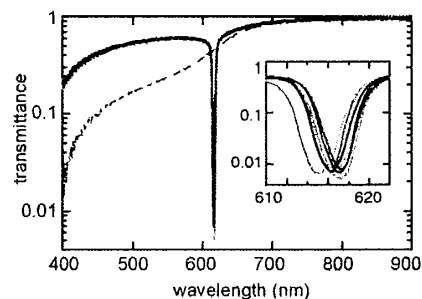


Figure 2. Transmission spectra of the crystal at various locations ($x = 0-30$ mm; see text). Inset shows an enlarged view around the dips.

Charged colloids, like hard-sphere colloids, may exhibit thermally driven crystallization due to a gradient in ϕ .³ However, this mechanism is inapplicable here since λ_B (and thus, ϕ) was practically uniform. The crystallization mechanism was examined by comparing the crystal growth curves with the time evolution of temperature distribution $T(x)$. Here, we used a sample with $T_C = 35$ °C ($>T_R$) and chose $T_0 = 40, 50,$ and 60 °C, whereby the growth rates clearly exhibited a dependence on T_0 . The growth rate increased with T_0 , as expected from the larger heat-conduction rate. $T(x)$ was measured using an array of thermocouples attached to the outer surface of the cell at 7-mm intervals. By assuming instantaneous crystallization at $T(x) = T_C$, we calculated the crystal length at various t . They show close agreement with the experiments for all T_0 , thereby suggesting that the present growth is attributed to a combination of heat conduction and thermally induced crystallization.

Heat conduction is a diffusion of thermal energy, which is mathematically equivalent to, but can be much faster than, mass diffusion. Thus, the growth rate of the present crystallization could be much larger than that due to Py diffusion at constant T ($<a$ few mm/h).^{2b} In the latter, the migration of particles during the growth period due to gravity and gradient of chemical potential may cause the non-uniformity in ϕ . The good uniformity attained in the present crystallization appeared to rely on its much faster growth rate.

References

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