Three-dimensional self-assembly by ice crystallization

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Three-dimensional self-assembly of colloidal particles by ice crystallization is observed in a water based-colloidal suspension. When water containing polystyrene beads freezes and is crystalized into ice, the polystyrene beads are extruded outward from the ice regions. Consequently, the concentration of polystyrene beads increases rapidly and they are assembled together into a regular structure. As ice crystallization proceeds, a color appears abruptly. This indicates that the polystyrene beads have been assembled three dimensionally. The generated three-dimensional structure is confirmed by scanning electron microscopy images and the existence of a photonic band gap measured by an ultraviolet-visible spectrophotometer. The sample fabricated by this method is compared with a sample made by conventional vertical deposition. © 2002 American Institute of Physics. [DOI: 10.1063/1.1483385]

Three-dimensional photonic band gap structures of the order of an optical wavelength have attracted a great deal of attention because of their potential use in various applications such as waveguides, filters, etc. Accordingly, intensive studies have been performed over the last few decades to fabricate three-dimensional regular structures. Typical methods using colloidal self-assembly are sedimentation of colloidal particles, vertical deposition and electrophoresis. All of these methods can fabricate three-dimensional photonic crystals by using different forces. The force of gravity is used in the first case, capillary force in the second, and Coulomb force is dominant in the last case. The method using capillary force could be adapted to assemble particles on large areas. To use capillary force, particles should be protruded from the surface of a solution. Generally, particles on the surface of a solution can be protruded onto a solid substrate by evaporating the solvent. However, we would like to accomplish this by freezing the solvent.

In this study, we report the phenomenon of polystyrene beads assembling three dimensionally when water containing polystyrene beads freezes. First, water containing polystyrene beads (about 220 nm) is placed between glass substrates, as shown in Fig. 1. If it is frozen from the bottom, ice will form from the bottom and polystyrene beads will move outward from the ice region. As water crystallizes into ice, the concentration of polystyrene beads increases and they are assembled mainly beneath the upper glass substrate. As they are assembled, a color appears abruptly, as shown in Fig. 2. The absorbance spectra, shown in Fig. 3, is measured with an ultraviolet-visible spectrophotometer. For the samples, the filled inverse triangles are fabricated by the vertical deposition method and the filled circles are made by ice crystallization.

When light enters the crystals at a normal incident angle, the photonic band gap generated by the vertical deposition method is about 530 nm and the band gap generated by ice crystallization is about 565 nm because of the difference in the media, air versus ice. The relationship among \( \lambda_{\text{max}} \) (the position of the first-order diffraction peak), \( \phi \) (incident angle), and the spacing (\( d_{111} \)) between (111) planes is given by the Bragg’s equation:

\[
\lambda_{\text{max}} = 2d_{111}(n_{\text{average}}^2 - \sin^2 \phi)^{1/2},
\]

\[
n_{\text{average}} = f_{\text{PS}}n_{\text{PS}} + f_{\text{Air}}n_{\text{Air}} + f_{\text{Ice}}n_{\text{Ice}},
\]

where \( n_{\text{PS}} = 1.59 \), \( n_{\text{Air}} = 1 \), \( n_{\text{Ice}} = 1.33 \), \( n_{\text{average}} \) is the average refractive index, and \( f \) is the filling ratio. We assume the packing density of polystyrene beads is 74% and the crystals have a cubic-close-packed structure. Therefore, \( d_{111} \) is \((2/\sqrt{3})D\) (\( D \) is the diameter of a polystyrene bead). In this equation, we can predict the average refractive index of the latter case (ice medium) will be larger than the former case (air medium) and thus \( \lambda_{\text{max}} \) of the latter is also larger than the former. Calculating \( \lambda_{\text{max}} \) using these equations, \( \lambda_{\text{max}} \) of the former is 525 nm and the latter is 550 nm.

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To examine the crystal structure made by vertical deposition and ice crystallization, we survey scanning electron microscopy (SEM) images, as shown in Fig. 4. The crystals assembled by vertical deposition are well ordered with monostructure on large areas, whereas the crystals assembled by ice crystallization have various ordered structures (planar, bending, and spherical structures) in local regions. The planar structure is dominant, while the other structures are spread out sporadically and the disordered polystyrene beads are scattered. These structures may be generated by the mechanism schematically illustrated in Fig. 5. As the rate of freezing (0.010 cm$^3$/s) is very fast, the water itself is not frozen independently, but rather it is frozen with the polystyrene beads. If the polystyrene beads are crystallized entirely within the water, a spherical structure is generated because it is the most stable from the standpoint of surface energy. As water changes into ice, polystyrene beads are extruded outward from the ice regions except for crystallized polystyrene beads within the ice. Therefore, the concentration of polystyrene beads is increased and they are assembled by capillary force. The beads crystallize in small domains in various places, but the small domains do not collectively assemble
because the rate of freezing is so fast that they do not have enough time to be assembled by lateral capillary force and to generate convective flow. Moreover, when water freezes, volume is increased and thus it imposes pressure on the crystals between the glasses and distorts the planar structure into bending structures. Therefore, if the rate of freezing is slow enough, the spherical structure will be replaced by the formation of planar structure on large areas. When the rate of freezing is $3.472 \times 10^{-4}$ cm$^3$/s, the planar structures are dramatically increased and are assembled among small ordered regions, as shown in Fig. 6, because there is sufficient time to be assembled by lateral capillary force and convective flow.

In summary, we fabricated a colloidal three-dimensional self-assembly by freezing water containing polystyrene beads. The generated structures by ice crystallization are planar, bending, and spherical shapes. These structures may be generated by the fast rate of water freezing and the planar structures are dramatically increased and are assembled among small ordered regions when the rate of freezing is decreased.

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