Colloidal Crystallization in Spherical Containers

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Colloidal crystals possess a photonic stopband as refractive index is periodically modulated in the structures. The stopband develops the colors through the reflection of selected wavelength of light when it is located in the visible. The structural colors are iridescent, never fade as long as the structure persists, and tunable by adjusting interparticle distance, which render the colloidal crystals promising for various coloration and sensing applications. However, a conventional film format of the crystals has low post-processability and reconfigurability, restricting the use. A granular format is expected to overcome the limitations of the film format. Furthermore, the granules, designed to have fluidic compartments containing colloidal crystals, potentially provide in-situ color tuning. To design such photonic capsules in a controlled manner, we have used droplet microfluidics. With a capillary microfluidic device, water-in-oil-in-water (W/O/W) double-emulsion drops are prepared, which are then used as a template to produce the photonic capsules. Innermost water phase contains colloidal particles to build colloidal crystals and middle oil phase is either photo- or thermo-curable monomer to form a stable polymeric membrane. To crystallize the colloidal particles in the innermost water phase, two opposite interparticle potentials of repulsion and attraction are employed, respectively.

Colloidal particles with surface charges have the repulsive potential due to electrical double-layer interaction. The particles spontaneously form non-close packed crystals in the core above a certain volume fraction by occupying the whole volume of the innermost phase. The colloidal crystals are formed by aligning the hexagonal array of crystals along the inner wall of the spherical core at an early stage, resulting in the isotropic photonic property. The crystals slowly evolve into a single crystal by rearrangement. The photonic capsules containing a single crystal have anisotropic photonic property as crystal planes that are aligned parallel to the wall are different depending on the location.

The attractive potential is achieved by depletion interaction. When the depletant is dissolved in the innermost phase in the presence of salts, attractive potential overwhelms the repulsive one. The depletion attraction leads to the formation of close-packed crystals, which results in many crystallites along the inner wall and no particles in the center. As the close-packed crystals coexist with the particle-depleted center, the volume change of each colloidal particle can lead to a change of lattice constant; this is difficult to achieve with nonclose-packed crystals prepared by repulsive potential. When the colloidal particles are composed of an insensitive core and temperature-sensitive shell, the crystallites in the core exhibit a drastic temperature-dependent color change.