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3D investigation on polystyrene colloidal crystals by floatage self-assembly with mixed solvent via synchrotron radiation x-ray phase-contrast computed tomography

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ABSTRACT

The floatage self-assembly method was introduced with mixed solvent as the medium of polystyrene sphere suspension to fabricate the colloidal crystal. The three dimensional (3D) void system of the colloidal crystal was noninvasively characterized by synchrotron radiation phase-contrast computed tomography, and the quantitative image analysis was implemented aiming to the polystyrene sphere colloidal crystal. Comparing with gravity sedimentation method, the three samples fabricated from floatage self-assembly with mixed solvents have the lowest porosity, and when ethylene glycol and water were mixed with ratio of 1:1, the lowest porosity of 27.49% could be achieved, that has been very close to the minimum porosity of ordered 3D monodisperse sphere array (26%). In single slices, the porosities and fractal dimension for the voids were calculated. The results showed that two factors would significantly influence the porosity of the whole colloidal crystal: the first deposited sphere layer's orderliness and the sedimentation speed of the spheres. The floatage self-assembly could induce a stable close-packing process, resulted from the powerful nucleation force-lateral capillary force coupled with the mixed solvent to regulate the floating upward speed for purpose of matching the assembly rate.

1. Introduction

Three-dimensionally (3D) periodic colloidal crystals fabricated from monodisperse silica or polystyrene (PS) microspheres have attracted great attentions for application in many fields, such as, photonic crystals (López, 2003), removable templates for 3D macroporous materials (Zhong et al., 2000; Yi and Kim, 2003; Zukalova et al., 2005), structural phase model (Gasser et al., 2001), and so on.

In various assembly techniques (Mayoral et al., 1997; Ye et al., 2001; Liu et al., 2005; Park and Xia, 1999), gravity sedimentation is a traditional and simplest approach for fabricating colloidal crystal. But its major disadvantage is the very little control over the morphology and the number of layers of the 3D crystalline array. In this method, layering may occur, which usually leads to the formation of a number of sphere layers of different densities and degree of order along the direction of the gravitational field (Xia et al., 2000). So many strategies were carried out to regulate the assembly process. Kumacheva showed that sedimentation under an oscillatory shear could greatly enhance the degree of order and the homogeneity in the resulting 3D array (Vickreva et al., 2000). By performing the experiment on a space shuttle, Chaikin eliminated the profound influence of gravitational field on crystalline structure to obtain a purely random hexagonal close packed structure at volume fractions up to 61.9% (Zhu et al., 1997). Actually, the gravity sedimentation method involves several complex processes such as gravitational settling, translational diffusion (or Brownian motion), and crystallization (nucleation and growth) (Xia et al., 2000). So the success of gravity sedimentation relies on tight control over the self-assembly process, in which the rate of sedimentation is a significant factor. The approach to regulate the rate of sedimentation could take various experimental parameters into account, such as, temperature, force field, size of the spheres, density of the solvent, concentration of the suspension, and so on. In this paper, we propose the thoughts of employment of mixed solvents with PS sphere suspensions in gravity sedimentation. The aim is to carefully tune the properties of the solvents, such as the density and viscosity, in order to regulate the rate of sphere sedimentation in the solvent for improving the morphology and orderliness of the resulting colloidal crystals. On the other hand, a previously presented in situ solvent evaporation method (Fu et al., 2009) illuminated that the self-assembly at air-liquid interface could induce colloidal crystal with large area and controllable number of layers. Thus, extending from gravity sedimentation with the mixed solvents aforementioned, we employ some kinds

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of mixed high-density solvents. Then the gravity could be overcome by floatage and the self-assembly will be achieved at the air-liquid interface of the suspension.

The common techniques for structure investigation of colloidal crystal generally fall in either surface methods or bulk averaging methods. As scanning electron microscopy aims to surface structure with disadvantage that no information about the internal sphere packing can be acquired (Fu et al., 2009; Blanco et al., 2000). Small-angle x-ray scattering (Hu et al., 2010) and transmission/reflection spectrum (Norris et al., 2004) provide the average information of the entire colloidal crystal structure but ignore the detailed arrangement such as the local defect, which is important for the optical properties and growth process of the colloidal crystal (Meng et al., 2006). To study the local structure in three dimensions, confocal microscopy (Gasser et al., 2001; Schall et al., 2004) were used by some studies for measurement of the colloidal particles. But the particles are required to be labeled to make them visible with fluorescence microscopy, and to prevent the scattering of visible lights, the space among the particles has to be infiltrated with a refractive index matching liquid (Gasser et al., 2001). That possibly impacts the grown crystal structure. Thus, a new technique should be introduced into the research field of colloidal crystal for studying the local internal structure in three dimensions. As a noninvasive and in-situ characterization technique, synchrotron radiation (SR) x-ray computed tomography (CT) is adopted firstly by our group to access the internal structure of colloidal crystals with detailed packing information. Moreover, for samples consisted of light element, such as polystyrene for colloidal crystal, the employed phase contrast imaging (PCI) method based on the high degree of (lateral) coherence of SR source could achieve satisfactory image contrast due to the sensitivity of light element to the wave phase, solving that the traditional absorption contrast makes low contrast.

In this paper, a floatage self-assembly with mixed solvent was proposed for assembly of PS colloidal crystal based on the characterization technique of SR x-ray phase-contrast CT and the following image process and analysis method. The influence of calculated sedimentation speed of the PS spheres in different mixed solvents on porosity of the colloidal crystal was investigated. The morphology evolution of the pores at different slices' positions was explored. And further the self-assembly mechanism for floatage self-assembly was discussed.

2. Materials and methods

2.1. Suspensions

Aqueous suspension of polystyrene sphere (2.5% solids, w/v) from Polysciences Inc. (U.S.A.) was labeled as s-H_2O. To fabricate PS sphere suspensions with different solvents, the original aqueous suspensions were set until the spheres settled down on the bottom of the containers, afterwards the water was extracted. Then equivalent volume of butanol, ethylene glycol or mixture of ethylene glycol and water was added in and labeled as s-BuOH, s-EG, or s-xEGyH_2O, respectively. Three kinds of mixture of ethylene glycol and water were used with different ratios of volume (x: y) and the corresponding PS suspensions were labeled as s-1EG2H_2O, s-1EG1H_2O and s-2EG1H_2O.

2.2. Self-assembly

To acquire a capillary as the self-assembly container, the top of a 10 μl pipet tip (Fisherbrand, China) was hot-melt, drawn and then sealed. Before assembly, the capillary was firstly immersed in absolute ethylalcohol and then dried in an oven. The suspensions were treated in an ultrasonic instrument for 10 min for uniform distribution of the PS spheres in the solvent. To assemble the PS colloidal crystals, drops of one suspension were added into the capillary, and then it was settled for sedimentation of the PS spheres under gravity or floatage. When the desired number of sphere layers was assembled, the solvent could be removed from top or bottom of the capillary.

2.3. Image acquisition for phase-contrast CT

The structure of fabricated colloidal crystals was characterized by SR phase-contrast CT at BL13W1 of Shanghai Synchrotron Radiation Facility (SSRF), which is a third generation synchrotron radiation facility with stable electron beam current of 210 mA and 3.5 GeV storage ring energy (Xie et al., 2015). For phase-contrast CT, the incident monochromatic x-ray of 12 keV was obtained through a Si(111) double-crystal monochromator, and then passed through the sample, which was mounted on an assembled 7-axis kohzu stage approximately 34 m from the wiggler source of the beamline. The transmitted x-ray beam was recorded by an x-ray sensitive detector with 200 μm thick YAG: Ce scintillator and PCO 2000 CCD (2048×2048 pixels). The sample-to-detector distance was 8 cm. For CT data acquisition, the data set contains 900 projections for a half-turn between 0° and 180° in 0.2° steps. The exposure time for each image was set for 5 s. Two flat field images were also captured between every 30° rotation and five dark current images were acquired at the end to normalize the projections.

2.4. Imaging process and analysis

The x-ray imaging detectors are sensitive to intensity modulations, the absorption and phase information can both be embedded in the acquired images, and the phase information cannot be accessed directly without any further processing. So it requires the phase-retrieval processing to extract the phase information for object identification. When the sample, such as PS spheres, fulfills the assumption on its properties: the absorption is weak and the sample is homogenous, the real and imaginary parts of n(x,*y*,z)−1 are proportional to each other:

$$\delta(x, y, z) = \varepsilon\beta(x, y, z)$$

where n is complex refractive index, the real part δ is refractive index responsive to the phase shift, the imaginary part β is absorption index, (x,y,z) is the spatial coordinates, and ε is a constant. That is the phase-attenuation duality (PAD) property (Paganin et al., 2002; Wu et al., 2005), which has been testified to work at the hard x-ray level (Chen et al., 2013, 2011; Guo et al., 2012; Arhatari et al., 2007; Langer et al., 2010). Based on the PAD property, the single sample-to-detector distance (SDD) phase-retrieval algorithms could be employed for extracting the phase information. In this paper, the phase-attenuation duality Paganin algorithm (PAD-PA) was used, which was proved to gain better density resolution in both statistical and structural noise study (Chen et al., 2013). PAD-PA provides a method to reconstruct the projected thickness t(x,y) of the homogeneous sample using a single defocused image by solving the transport of intensity equation, thus it simultaneously extracts phase and amplitude information.

For slice reconstruction, the FFT-based algorithm of Gridrec was employed. Compared with the common filtered back-projection (FBP) algorithm, the Gridrec algorithm has reduced the reconstruction time for 650×650×515 datasets from several hours to less than ten minutes, according to Dowd's experience (Dowd et al., 1999). The performance and reconstruction accuracy of Gridrec was also further testified (Marone et al., 2010).

So the PITRE V3.1 software was adopted with PAD-PA for phase retrieval and Gridrec algorithm for slice reconstruction. Meanwhile, the Shepp-Logan filter was utilized to suppress noise; the ring artifact correction was also carried out. Then, the voids of colloidal crystal were segmented by threshold, which was selected according to the known diameter of the PS sphere. Rendering for 3D structure of the PS sphere array was realized by software Amira. Analysis for voids among the PS spheres was performed by software Blob 3D (Ketcham, 2005), that