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A facile strategy to colloidal crystals by drying condensed suspension droplets

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ABSTRACT

Drying condensed colloid suspension droplet on a horizontal glass substrate has been developed as a simple strategy to fabricate highly-ordered colloidal crystals. A uniform film obtained at above room temperature possessed a face-center-cubic (*fcc*) crystalline structure and excellent photonic properties. It was found that raising the drying temperature has resulted in a reduction in the lattice spacing of *fcc* colloidal crystals. The formation reason of uniform *fcc* colloidal crystals was directly related to the high drying temperature and the large colloid concentration. A ring-shaped stain generated by drying at room temperature has exhibited other highly-ordered microstructures with colloidal crystals, such as body center cubic (*bcc*) structure.

1. Introduction

Controlling the distribution of solute during drying is vital in many industrial and scientific processes, such as printing, biology and complex assembly [1,2], where segregation effects are usually undesirable in either of these cases. Evaporating droplets of particle suspension at room temperature (~25 °C) with a concentration lower than 1 wt.%, leaves frequently behind a ring-shape deposition of disordered particles, known as the coffee-ring effect [3–6]. It is noted that the ability to deposit particles uniformly is highly desirable in many applications [7,8]. Unfortunately, most proposed methods for avoiding the coffee-ring effect are costly in manufacturing or require long multistage processes. Herein, we present a facile and scalable strategy to realize a uniform deposition of colloidal particles by simply drying condensed suspension at above room temperature. More importantly, this low-cost approach is able to create colloidal crystals with highly-ordered structures. Colloidal crystals have attracted intense scientific interest because of their potentials in phonics, biomaterials, catalytic supports and lightweight structural materials [9–11]. Numerous techniques have been successfully developed to fabricate colloidal crystals, including spin-coating [12,13], vertical deposition [14,15], sedimentation [16], controlled solvent evaporation [17] and so on. In spite of that, more general and practical strategies to colloidal crystals are still desirable.

In optics, three-dimensional (3D) colloidal crystals are particularly important as they can be used as photonic crystals for manipulating the transmission of light *via* a photonic band gap. Artificial 3D colloidal crystals obtained predominantly have a face-centered cubic (*fcc*) crystalline structure, which is energetically favorable. The self-assembly of colloidal particles can easily achieve the closed-packed *fcc* structure of colloidal crystals, but it is still a problem to control the spacing parameter of *fcc* lattices. In comparison with the *fcc* structure, the body-centered cubic (*bcc*) structure of colloidal crystal possesses a lower packing fraction, which is also helpful for broadening the photonic band gaps. Although this structure of colloidal crystals has been prepared by electrophoretic deposition [18], or plasma etching method [19], the *bcc* structure is not energetically favorable for fabrication by the colloid self-assembly method. Because of this reason, only a few researchers have made progress toward this goal [20]. In this contribution, colloidal particles distributed in water are uniformly deposited through drying 7.5 wt.% suspension droplet at 30 °C on a horizontal substrate. The uniform film obtained shows a microstructure of *fcc* colloidal crystals and possesses excellent photonic properties. The lattice spacing of the uniform colloidal crystal is found to decrease gradually with the drying temperature increasing from 30 to 60 °C. Uniform deposition by drying condensed suspension at above room temperature is independent of the colloid types: polystyrene (PS) or silica colloids. Drying 1.5 wt.% suspension droplets at 25 °C yields a ring-like deposition of particles which is composed of large-area colloidal crystals with a *bcc* structure.

2. Experimental section

2.1. Preparation of PS colloids

Styrene and methyl methacrylate were distilled before use. Potassium persulfate was chemical graded reagents and used as received. The monodispersed PS submicron-sized spheres were syn-

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thesized by emulsifier-free emulsion polymerization, according to a literature method [21]. Deionized water (40 g) was poured into a reactor, and the water was kept at a temperature of 70 °C and stirred at 750 rpm. Styrene monomer (7.50 g) and methyl methacrylate (0.45 g) as an inhibitor were inserted into the solution. After 1 h, 2.5 g aqueous solution of potassium persulfate (0.07 g) as an initiator was introduced into the solution, and finally polymerization was performed under 70 °C and stirred at 750 rpm for 2 h. The average diameter of as-prepared PS colloidal particles is 226 nm with a monodispersivity less than 5%, measured by Zetasizer (Nano ZS90, Malvern).

2.2. Deposition of colloidal particles and characterization

The glass slip as a substrate was cleaned in acetone followed by deionized water with ultrasonic agitations, and then treated with a 3:1 mixture of concentrated sulfuric acid and 30% hydrogen peroxide to obtain a hydrophilic surface. A surfactant-free suspension droplet with a setting colloid concentration was extracted carefully to spread onto the horizontal cleaned substrate and dried at a given temperature. All drying experiments were performed under a relative humidity of 65–70%. Field-emission scanning electron micrograph (FESEM, S-4800, Hitachi Co., Japan) and UV–visible-NIR spectrometer (Cary 5000, Varian Co., US) were employed to characterize the morphology and photonic properties of colloidal crystals, respectively. Optical photographs of colloidal crystal films were made by camera (FUJIFILM, S2000HD). In addition, the weight loss during drying process of droplet was followed by TGA (Pyris 1 TGA, PerkinElmer Co., US) to shed light on the evaporating process of solvent.

3. Results and discussion

3.1. Uniform deposition of colloidal particles

To produce uniform films, the drying temperature and the colloid concentration are respectively adjusted with keeping other conditions constant. When the drying is carried out at room temperature (25 °C), solvent evaporation from a dilute colloid droplet (1.5 wt.%) creates a ring-like deposition (Fig. 1A), whose center region emerges some loosely-packed particles with an average diameter of 226 nm (insert). Drying a condensed suspension (7.5 wt.%) at 25 °C yields still a ring-like stain with a larger width (Fig. 1B), with disorderly-stacked colloidal particles in center region (Fig. 1B insert). At a higher temperature (such as 30 °C), evaporating solvent from 1.5 wt.% colloid droplet generates a white ring besides of outer colored ring (Fig. 1C), which is arrayed by quasi-ordered polymer spheres (Fig. 1C insert). If the colloid concentration was raised to 7.5 wt.%, drying this condensed suspension droplet at above room temperature (30 °C) could fabricate an even film with a green color (Fig. 1D). This colored film is relative uniform packed with orderly-arrayed colloidal particles (Fig. 1D inset), with a maximum thickness of 30.2 μm close to edge (Fig. S1).

A suitable concentration range of colloid is in 3.0–15 wt.% for even deposition of colloidal particles by drying at 30 °C (Fig. S2). With a weight fraction of 7.5 wt.%, the uniform deposition of colloids admits the drying temperature varying in 27–65 °C. To further realize the effect of processing parameters on dried patterns, a simple phase diagram is drawn through altering drying temperature and colloid concentration (Fig. S3). It is found that the uniform depositions are formed in moderate ranges of temperature and concentration. In addition, the uniform films could also be altered in size from 2.2 to 20 mm through drying droplets with these corresponding sizes at 30 °C (Fig. S4). Also, the uniform deposition by this strategy seems be independent of the size of submicron colloidal particles.

3.2. Microstructures and photonic properties of uniform film

The uniform film obtained at 30 °C with 7.5 wt.% is further observed by FESEM technique. From Fig. 2A, it is observed that the surface of resultant film parallel to the substrate is formed by highly-ordered hexagonal-packed colloidal particles in large area. A side of the cleaved film in Fig. 2B exhibits two hexagonal arrays and one square arrangement of colloidal particles, hinting that the resultant colloidal crystal has a *fcc* structure. According to *fcc* crystalline feature, these planes with hexagonal-packed particles (including one parallel to substrate surface) are recognized by (1 1 1) facet, while the plane with a square-packing of colloids should be (1 0 0) type facet, as marked in Fig. 2B.

Due to the highly-ordered structure, the uniform film obtained at 30 °C with 7.5 wt.% appears purple, red and green colors when the viewing angle is tilted from glance to normal (Fig. 3A). In Fig. 3B, the spectrum of uniform film obtained at 30 °C with 7.5 wt.% displays three groups of reflectance peak, evidently different from that of the disordered film. As for the *fcc* colloidal crystal, the relation between the reflection peak position and the viewing angle can be modeled by the Bragg–Snell law [22,23],

$$\lambda = 2d_{(hkl)}\left(n_{eff}^2 - \sin^2\theta_{(hkl)}\right)^{1/2} \quad (1)$$

where λ is the wavelength of radiation in a vacuum, $d_{(hkl)}$ is the interplanar spacing for a (hkl) crystallographic plane, and n_{eff} is the effective average refractive index of the polystyrene-air medium, $\theta_{(hkl)}$ is a angle between the reflectance light and the normal to the (hkl) plane. The effective refractive index n_{eff} can be expressed as:

$$n_{eff} = n_{PS}f_{PS} + n_{air}(1 - f_{PS}) \quad (2)$$

where n_{PS} and n_{air} are refractive indices of polystyrene and air, respectively, and f_{PS} is the volume fraction occupied by polystyrene spheres in the crystal film. Since $n_{air} \approx 1.0$, $n_{PS} \approx 1.5$ and $f_{PS} = \pi/(3\sqrt{2}) \approx 0.74$ for a close crystalline packing of *fcc* crystal structure [24], we can estimate n_{eff} to be 1.37.

For the (1 1 1) plane parallel to the crystal film surface,

$$d_{(111)} = a(2/3)^{1/2} \quad (3)$$

where a is the lattice parameter. With $\theta_{(111)} = 0°$ for a normal observation, the reflection peak position is at 531 nm seen from Fig. 3B. According to Eqs. (1) and (3), the lattice parameter a of (1 1 1) plane is estimated from the normal reflection peak to be 237.5 nm, which is slightly larger than the average diameter of spheres (226 nm). This may prove that the PS particles in crystals are not in physical contact but that they might construct a periodic array among a dispersion media. Besides, the reflection in the 324–349 nm range is also predicted when $\theta_{(111)}$ is near to 90°. In case of the (1 0 0) plane, $d_{(100)} = a$, when $\theta_{(100)} = 25°$, a reflectance peak is calculated in term of Eq. (1) to be at 619 nm, which is perfectly consistent with the result of spectrum (620 nm).

3.3. Effect of drying temperature on microstructure of uniform film

With the temperature increasing from 30 °C, drying 7.5 wt.% suspension droplets can still fabricate uniform films with same colors and similar microstructures. Nevertheless, these reflectance peaks of dried films obtained shift towards short wavelength as the drying temperature increases (Fig. 4A). Calculated from these reflectance peaks, the lattice parameter is found to decrease finely from 237.5 to 231.2 nm with the drying temperature from 30 increasing to 60 °C (Fig. 4B). As shown in inset of Fig. 4B, the lattice