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Rapid fabrication of large area binary polystyrene colloidal crystals

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A B S T R A C T

Binary colloidal crystals (BCCs) possess great potentials in tuning material and optical properties. In this paper, the combination of interface transferred method and spin-coating method is used to fabricate BCCs with different patterns via controlling the size ratio of small (S) to large (L) colloidal spheres and the spin speeds. It is found that BCCs formed LS_2, LS_4 and LS_6 by changing the size ratio. In addition, there are some new and complicated structures, such as LS_{12}, Janus arrays, formed at the low spin speed. This simple assembly method has potential to allow for the creation of optical metmaterials and the plasmonic structures with chiral optical properties.

1. Introduction

Monolayer colloidal crystals had received ongoing attention and wide applications in optoelectronic devices and surface-enhanced Raman scattering, sensors, super-hydrophobic surfaces and light emitting diode for several decades [1–5]. Nevertheless, the colloidal crystals restrict their further development in 3D photonic crystals due to the limitations of single structures. Recently, some works have focused on fabrication of BCCs consisting of colloidal spheres with two sizes, which could exhibit many more advantages compared with single-sized colloidal spheres due to the structural diversity. So, all kinds of self-assembly methods have been developed for constructing binary colloidal arrays: layer by layer growth, controlled drying, accelerated evaporation, air/water interface self-assembled [6–9]. In these methods, the quality of BCCs is determined by the size ratio and concentrations of large and small particles solution. Therefore, the fabrication of the BCCs still remains a great challenge for further applications to a large extent. In addition, wang et al. presents the stepwise spin-coating method to fabricate 3D BCCs with LS_2 and LS_3 structures by manipulating the size ratio and the spin speed [10]. This method hardly depends on the concentrations ratio of large and small particles. However, the uniformity and quality of first PS crystals is difficult to control by spin-coating process.

In this paper, the combination of interface transferred method and spin-coating method are used to prepare large scale well-ordered BCCs. That is to say, first monolayer PS arrays are prepared by the interface transferred method. This method may not only provide large area and high quality PS arrays but also they can be transferred to any needed substrate. Different

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patterns of the BCCs formed by controlling the diameter ratio of large and small spheres and the spin speed during spin-coating process. It is found that BCCs with LS_2, LS_4 and LS_6 LS_{12} and Janus arrays can be fabricated at different size ratio and spin speed. The mechanism of BCCs is further discussed in detail.

2. Experiments

2.1. Materials

Glass slides cutted as 10 cm × 10 cm pieces were immersed in a mixture solution of 98% H_2SO_4 and 30% H_2O_2 with a volume ratio of 2:1 for about 12 h, then were rinsed completely with deionized water and dried with the stream of nitrogen. Then, indium tin oxide (ITO) substrates were cleaned for 0.5 h in acetone, isopropyl alcohol and absolute ethanol in sequence by ultrasonic cleaner. The PS spheres with the diameter 200, 500, 750 and 1000 nm and the concentration of all PS sphere is 2.5 wt% were purchased from Alfa Company (www.alfachina.cn).

2.2. Fabrication of monolayers large PS colloidal spheres

PS spheres with 500, 750 and 1000 nm diameters were used to prepare of 2D monolayer PS arrays via the interface transferred method [11]. The method involved three processes: a given volume of water drops on the glass substrate and spread to the whole one. After injecting the PS colloidal suspension with the concentration of 2.5 wt% into water surface, the PS spheres are spread and move freely on the water surface within several minutes due to Brownian motion. When aqueous solution evaporated completely, PS spheres are random distribution on the substrate. Step 2: when the substrate is immersed in water along specific angle, the random PS spheres detached from the glass substrate and floated on the water interface. At the same time, the random PS spheres self-assembled in a dense monolayer PS arrays on the water interface under surface tension. Step 3: monolayer PS spheres arrays that floated on water surface can be picked up by ITO substrate, which is called as "receiving substrate". ITO substrate slowly withdraws at about 30° and monolayer PS arrays attached to the substrate surface. The sample dries in a natural environment. Finally, the monolayer PS arrays form on the ITO substrate.

2.3. Fabrication of binary colloidal arrays with different patterns

The sample is annealed at 60 °C temperature for 1 h in room-temperature oven. It is an important and key step to fabricate bCCs. After solidified dealing, the large PS mask cannot easily be destroyed by 200 nm PS droplets solution during the next spin coating process. Small-size PS spheres suspension with 200 nm diameter and the concentration of 2.5 wt% drops on the monolayer 2D colloidal arrays of large sphere. At different spin speed, the bCCs with various patterns formed on the ITO substrate. The sketch is shown in Fig. 1.

2.4. Characterization

Surface morphologies of bCCs were recorded using a JEOL JSM-6700F field-emission SEM (FESEM) operated at 5 KV and the sample were sputtered with 20 nm Au film.

3. Results and discussions

The structure patterns of binary colloidal arrays highly depend on the diameter ratio (γ) of large sphere and small one. To demonstrate the influence ofγon the patterns of BCCs, a 2D hexagonal closed PS colloidal arrays with the size of 500, 750 and 1000 nm were prepared by the interface assembling approach. Compared to other assembly method, such as, spin-coating, L-B, dip-coating and layer by layer method [12–15], the interface assembling approach is the most simple and effective for preparing the large area monolayer PS arrays. In fact, the quality of below PS colloidal arrays plays an important role to

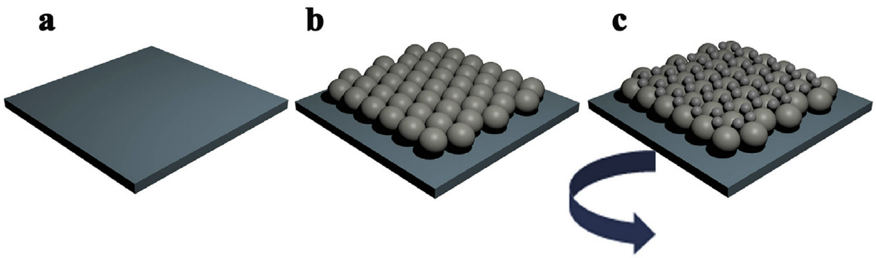

Fig. 1. The process illustration for the fabrication of binary colloidal crystals via combination interface-transferred method with spin-coating: a ITO substrate; b monolayer large PS arrays; c binary colloidal crystals.