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ORIGINAL CONTRIBUTION

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Complex aggregates of silica microspheres by the use of a polymer template

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Abstract Evaporation of a droplet of silica microsphere suspension on a polystyrene and poly(methyl methacrylate) blend film with isolated holes in its surface has been exploited as a means of particles self-assembly. During the retraction of the contact line of the droplet, spontaneous dewetting combined with the strong capillary force pack the silica microspheres into the holes in the polymer surface. Complex aggregates of colloids are formed after being exposed to acetone vapor. The morphology evolution of the underlying polymer film by exposure to acetone solvent vapor is responsible for the complex aggregates of colloids formation.

Keywords Colloids self-assembly · Solvent inducement · Polymer film dewetting

Introduction

The formation of highly ordered colloidal crystals has been a research focus over the past several decades for the potential applications, including photonic crystals, size-exclusion chromatography, enhanced catalytic reactivity, and sensors [1–4]. There are two main subjects on the formation of colloidal crystals. One is the fabrication of 3-D and 2-D structure with low concentration of defects. Many elegant approaches have been developed to obtain colloidal crystals over large areas, such as the famous vertical deposition [5] and the fluidic cell method [6]. The other is the fabrication of complex colloidal aggregates at the micrometer scale. However, relatively few approaches exist for controlling the aggregation and structure of colloidal clusters with small numbers [7–14]. Colloidal clusters with regular shape and size can be used in the theoretical research of hydrodynamic and optical properties of colloids having nonspherical morphologies [10, 11]. Spatial confinement is the most common method to direct the crystallization of colloidal particles [10–12, 15–17]. Electrostatic forces are also effective in obtaining regular clusters of microspheres [8, 9]. In addition, flat substrate patterned with different surface properties is also capable of fabricating good colloids aggregates [13, 18–21]. Once a droplet of colloidal suspension is put on a structured surface, the particles move to certain sites under the capillary force and/or various interaction. In our experiments, we use polystyrene (PS) and poly(methyl methacrylate) (PMMA) film with holes in its surface as the template. Silica microspheres are selectively packed into the holes of PS and PMMA blend film during the retraction of a droplet of suspension. Complex aggregates are thus obtained using clusters of microspheres in holes of polymer film as building blocks the exposure to acetone vapor. The movement of the colloids clusters is driven by the morphological evolution of the underlying poly-

mer film induced by the exposure to acetone vapor. The proposed approach is a promising route to form more complex colloidal structures which may exhibit interesting photonic properties [10, 11].

Experimental

Materials

Monodisperse silica microspheres with mean diameters of 375 nm were prepared by the Stöber method [22]. Standardized PS and PMMA used in this study were purchased from Aldrich Chemical Company with a reported mass, Mw(PS) = 200,000 and Mw(PMMA) = 100,000 g/mol (GPC), and polydispersity, Mw/Mn (PS&PMMA) = 1.03–1.06.

Preparation of PS/PMMA film with holes

Four weight percentage of PS and PMMA solution with weight ratio of 5/1 was cast onto a freshly cleaved mica substrate by microinjector. The solvent evaporation rate of the samples was controlled at 1.0 l/min [23]. Thus holes were formed on the blend film owing to convection.

Filling colloids into the holes in the surface of PS/PMMA film

Silica microspheres were dispersed in a mixture solvent of water and ethanol (3/1 v/v) or in pure deionized water. The typical concentration was 0.5–2 wt%. A 2 μl drop of certain suspension was deposited on the surface of PS/PMMA film at room temperature. Ultrasonication was employed to improve the regularity of the colloids packing in those holes. After the complete evaporation of the solvents, a ''coffee-ring'' of solid silica was formed on the PS/PMMA film and microspheres were packed into those holes of certain areas.

Treatment with acetone vapor

The PS/PMMA film with silica microspheres in the holes was exposed to saturated acetone vapor in a closed vessel at room temperature for various times. The sample was then removed to ambient atmosphere and dried to remove the remaining solvent. In order to capture the transitional state of the morphologies evolution, the exposure and characterization were performed on a same sample for several cycles. It is found that the treatment time less than 30 min have little influence on the morphologies.

Characterization

The morphologies of the 3-D colloidal crystals were characterized by the ESEM FEG Scanning Electron Microscope (Micro FEI PHILIPS). The ESEM was operated with an accelerating voltage of 20 kV and a pressure of ~5 Torr. All samples prepared for ESEM studies had been coated with thin layers of gold (~50 nm thickness). The drying process of a droplet of silica microsphere suspension on the PS/PMMA film was observed under a light microscope (LEICA DMLP) in reflection mode with a CCD camera attachment and a video recorder system. The surface topography of samples was measured at ambient conditions by atomic force microscopy, using a SPA-300 HV with a SPI3800N controller (Seiko Instruments Inc., Japan) in the contact mode. The probes used were standard 200-μm-long V-shaped Si_3N_4 cantilevers with narrow legs (nominal spring constant 0.02 Nm^{-1}, nominal tip radius 20–50 nm). Since the size of the AFM probe tip is much smaller than that of the microspheres or the holes in the polymer surface, the tip geometry has little influence on the obtained morphology [24, 25]. The scan speed was about 1 Hz. The contact angles of silica microsphere suspension on PS/PMMA film were estimated by Drop Shape Analysis DSA 10 (Krüss GmbH, Germany) at the ambient temperature. Water droplets (about 5 mg) were dropped carefully onto the films.

Results and discussion

Packing silica microspheres into the holes

Polystyrene and poly(methyl methacrylate) are strong immiscible blend systems. Phase separation will occur due to the convection effect by solvent evaporation [23, 26], which resulted in the formation of holes, consisting of PS, on the film surface (Fig. 1a). The surface of PS/PMMA film is covered with a PS-rich phase due to its slightly lower surface free energy with respect to the PMMA component. The water contact angle of the PS/PMMA film is about 105°, larger than that of a flat PS film (about 91°), because the PS/PMMA film has a very rough surface with respect to the flat PS film [27].

The drying process of a droplet of pure solvent or suspension containing colloids have been investigated by many groups [13, 21, 28–38]. The three-phase contact line of a droplet of pure solvent exhibits stick-slip motion during its evaporation on a flat substrate [28, 33]. In contrast, the contact line of a droplet of suspension can be easily pinned due to the presence of the particles and the initial roughness or chemical heterogeneities of the substrate [31–33]. In this case, a ''coffee-ring'' will form after the complete evaporation of the solvent [31, 32]. Multiple ring can be formed in some cases [33].

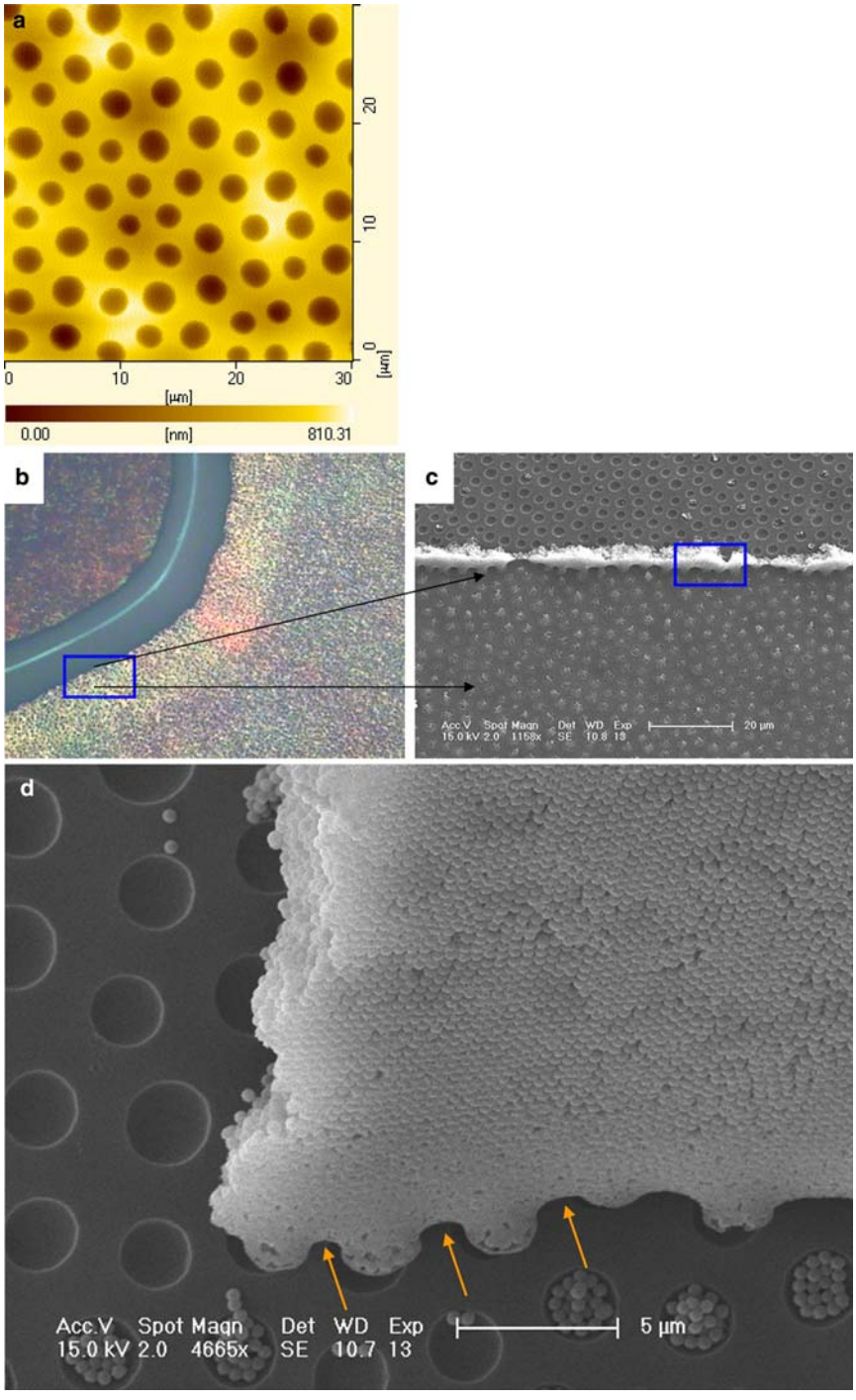

Fig. 1 **a** AFM height images of the original PS/PMMA film with holes in its surface. **b** Optical micrograph showing the partial ring formed on the PS/PMMA film surface after a droplet of silica microspheres suspension was dried. A *blue circle* in the middle of the ring can be seen clearly. **c** ESEM micrograph showing that the colloids selectively packed in the holes during the retraction. The silica microspheres ring has been peeled off and only partial perimeter is remained. **d** High magnification shows the good crystallinity of the "coffee-ring"

Furthermore, when a sessile droplet of suspension is dried on a patterned substrate, microspheres in the suspension can be selectively packed in certain areas during the movement of the contact line [13, 21, 35, 36]. We use this idea to crystallize silica microspheres into the holes in the PS/PMMA film surface.

When the silica microspheres aqueous solution is spread on the PS/PMMA surface, the contact line remains fixed for several minutes, and then retracts slowly as the droplet shrinks because of the uniform slow evaporation throughout the liquid/gas interface due to the high contact angle [13, 32, 34]. Along with the solvent, silica microspheres are selectively packed into the holes of the polymer film and nearly no particle is adsorbed on the surface while the contact area of the droplet decreases [29]. During the evaporation, the

concentration of the microspheres steadily increases, which, in turn, increases the chance of the contact line pinning. In order to obtain large area of silica microspheres clusters in the holes of polymer film, the pinning of the contact line of the droplet should be avoided or delayed. The microspheres in the droplet start to aggregate when the concentration of microspheres reaches a critical value; that is, the contact line is pinned [21]. Such pinning of contact line will induce the outward flow of the inner suspension and finally form a thick silica microspheres ring on the polymer film. For comparison, we add ethanol to the suspension to reduce the contact angle of the drop on the polymer film to about 70°. The droplet of such low contact angle forms a thinner liquid layer at the three-phase contact line. Thus, the periphery of the droplet dries much faster than its center. Combined with the strong pinning due to the solute microspheres, the contact line can easily be pinned during its retraction. Samples for further treatment are all made from silica colloids suspended in pure water.

When the receding contact line meets the holes, it becomes pinned at the periphery of these holes and pulls back from the nonwetting PS film, which induces the suspension to flow out of the hydrophobic PS surface and into the holes in the polymer film [13]. The dewetting between the suspension and PS film can be proved by the arches between adjacent holes at the periphery of the ring (indicated by the arrows in Fig. 1d). During the retraction of the droplet on the PS/PMMA film, the capillary force is sufficiently strong to push the colloidal particles into the holes in the polymer surface, and left nearly no microspheres on the top surface of the film [10]. If the concentration of microspheres dispersion was high enough, each hole would be filled with the maximum number of silica microspheres as determined by geometrical confinement (Fig. 1c). The microspheres within each hole tended to be in compact contact as a result of attractive capillary force caused by subsequent solvent evaporation in each hole [39].

On the other hand, the finally formed silica microspheres ring has good crystallinity (Fig. 1d). So this approach has another potential application in fabricating high-quality 3-D colloidal crystals with large area. It is interesting to observe that there is always a blue circle in the middle of the silica microspheres ring under optical microscopy. The ring can be peeled off by vibration or using tape, and only the holes within the blue circle are filled with microspheres. Other holes out of the circle are only partially filled with microspheres

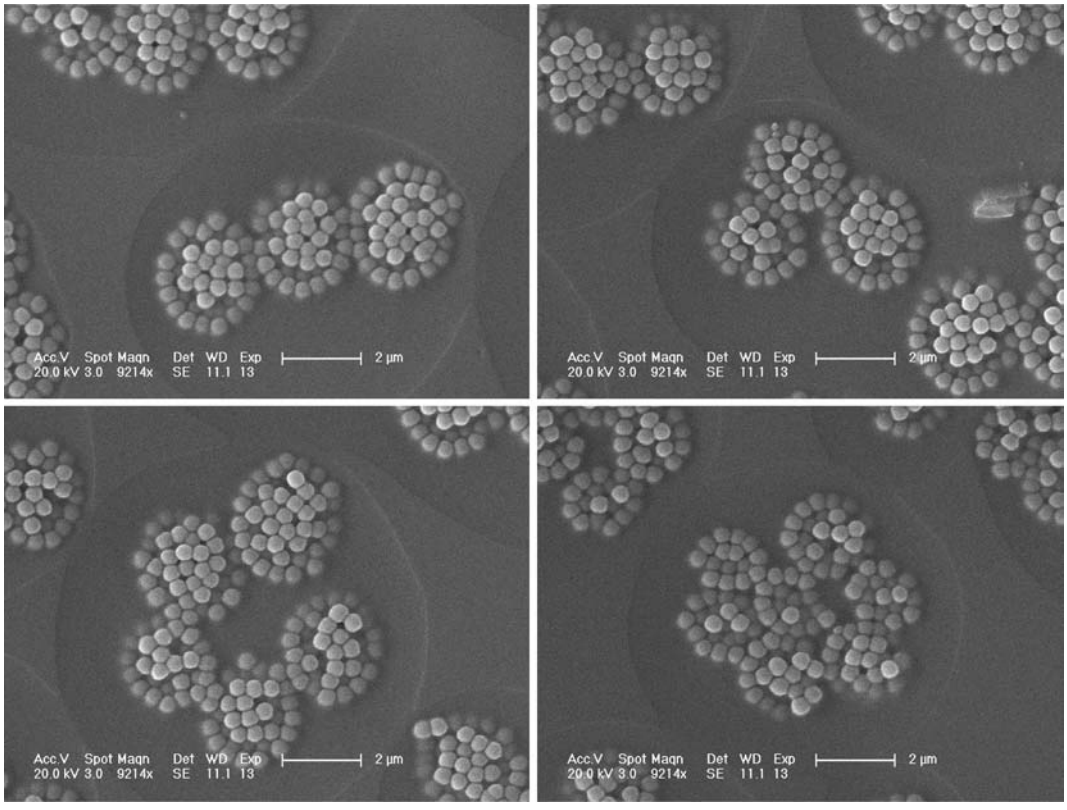

Fig. 2 ESEM micrographs of the different complex aggregates of silica microspheres on the same PS/PMMA film surface after treated by acetone vapor for 1 h

because of the dewetting between silica microspheres suspension and PS film. So the color of the circle is probably caused by the close packing of colloids at certain areas.

Formation of complex colloids aggregates

The morphology of the blend polymer film can preserve without notable change during the deposition because water and ethanol are nonsolvent for PS. However, after exposure to saturated vapor of acetone for 1 h, complex aggregates of microspheres were formed on the polymer film at different place (Fig. 2). The various numbers of colloidal clusters in these aggregates resulted from the random distribution of the holes in the surface. In order to investigate the mechanism for the formation of these complex aggregates, the evolution of PS/PMMA film with microspheres in its holes during the treatment of acetone vapor was tracked. Figure 3a shows morphologies of PS/PMMA film at the transitional stage in the course of the vapor exposure. It can be seen that the holes in the surface of the PS/PMMA film expand and some coalesce with adjacent holes after the treatment. On the other hand, the middle point of adjacent holes turns to be the deepest position of the coalescent holes (Fig. 3b). The depth of holes in the original PS/PMMA film is about 500 nm. After being treated with acetone vapor for 45 min, the holes in the polymer film become much shallower and expand simultaneously. After being treated for another 45 min, the adjacent two holes almost coalesce with each other. Another treatment of 60 min results in the complete coalescence of adjacent holes. In this example, we show the process of the coalescence of adjacent two holes. In fact, adjacent holes of other number can coalesce with each other in the same way.

The above results lead us to bring forward a probable model for the system upon solvent treatment, which is shown in Fig. 4. The original holes are all separated in the polymer surface. As the contact line of the droplet recedes, silica particles are drawn with the fluid to pack into the holes, where subsequent evaporation allows colloidal crystals to form colloidal crystals induced by strong attractive capillary forces between individual

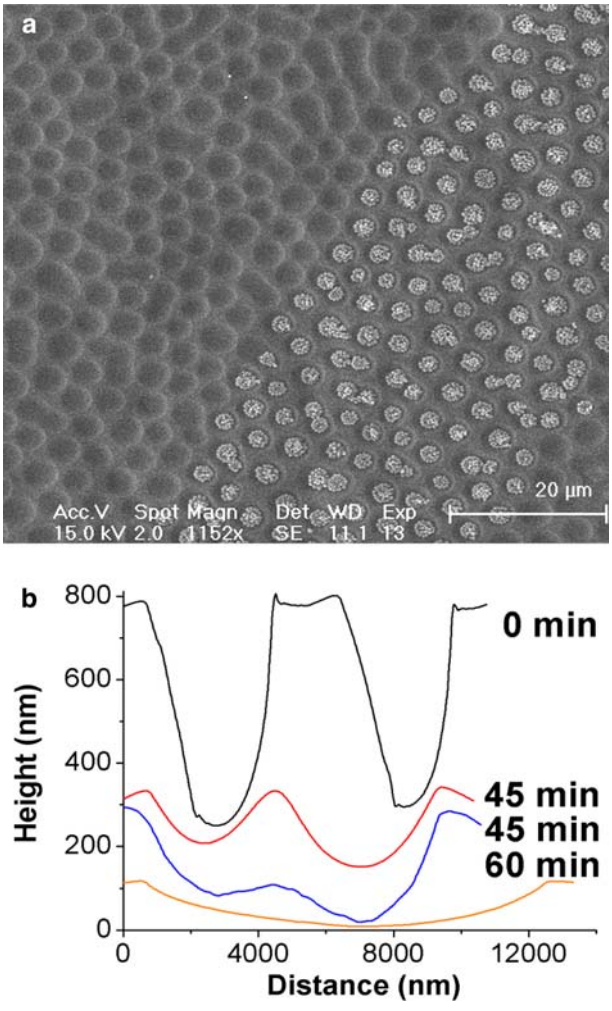

Fig. 3 **a** ESEM micrographs of transitional state of the evolution of PS/PMMA film with colloids in its holes after treated by acetone vapor for about 45 min. **b** The superimposed cross section of AFM topographic images of the two adjacent holes at different states of the solvent vapor treatment (time of each treatment shown near the curves). These curves have been scaled to a constant height, and vertically offset for clarity

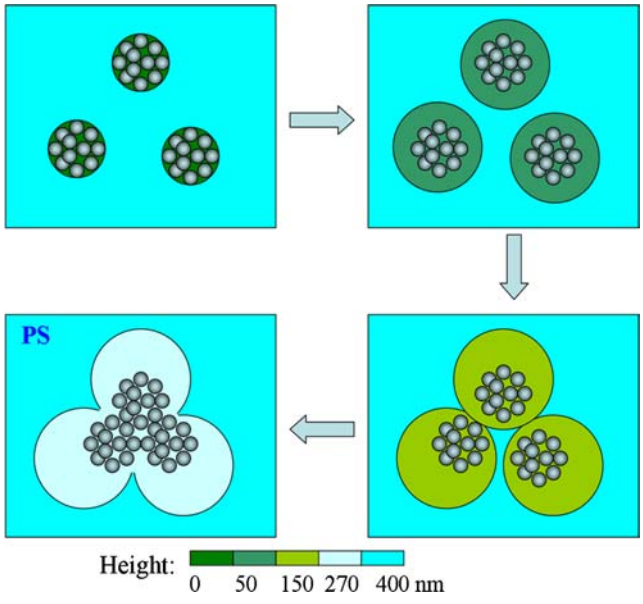

Fig. 4 Schematic mechanisms of the formation of silica microspheres complex aggregates during exposure to acetone vapor

microspheres. However, during the solvent annealing for certain time, sufficient acetone enters the PS film to cause the T_g of PS to drop. Therefore, the PS film is highly mobile and can reconstruct itself easily [40]. The diameters of those holes increase and adjacent holes ultimately coalesce with each other. These colloidal crystals remain in their shape during the evolution of the underlying polymer film. Considering the dewetting between the silica particles and PS and the gravitational force, the colloidal clusters in adjacent holes will compose larger aggregates at the center of the coalescent holes. It is worth noting that the holes become shallower during the exposure to acetone vapor. With careful control, the complex aggregates can be made on a flat polymer film.

After solvent annealing, the surface of colloidal crystal is covered with PS thin film. The water contact angle of the surface of colloid crystal is about 91°, almost equivalent to that of PS (about 89°). This migration of PS occurs because of its lower surface energy and high mobility during the solvent annealing [40].

Conclusions

In summary, we have shown that aggregates of colloids can be fabricated when the PS/PMMA film with holes is used as the carrier. By choosing proper solvent, we can control the drying process of a droplet of silica suspension on the polymer surface. Microspheres can be selectively packed into those holes in the polymer surface during the retraction of the droplet. This new approach is very simple and carries potential for packing colloids to form various clusters on different patterned substrates. The colloidal clusters in holes then act as building blocks to form complex aggregates during the morphological evolution of PS/PMMA film induced by the treatment of acetone vapor.

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