Rings of Nanoparticle-Decorated Honeycomb-Structured Polymeric Film: The Combination of Pickering Emulsions and Capillary Flow in the Breath Figures Method

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The self-assembly of nanoparticles at the fluid/fluid interface (Pickering emulsions) in the breath figures (BF) method have been explored to direct nanoparticles onto BF microarrays and adjust the BF assembly in microsize. Circular rings of nanoparticle-decorated honeycomb-structured polymeric film can be obtained by a one-step process. The combination of Pickering emulsions and capillary flow in the BF method may be responsible for the formation of this intriguing structure.

Introduction

Fabrication of ordered arrays of inorganic nanoparticles with tailored properties is of paramount importance to applications in diverse fields.[1–3] The spatial organization of nanoparticles is recognized as a fundamental way to exploit the size-dependent behavior of the individual nanoparticles as well as to yield striking collective properties.[4,5] However, directing the deposition of nanoparticles onto specific regions of surfaces with high selectivity and ease still poses a significant challenge. Various methods have been applied in order to manipulate the organizational geometry of nanoparticles. These approaches usually involve photolithography and soft lithography, which are complex and time-consuming.[6,7] Moreover, in the case of guided-assembly of particles on patterned templates, which has attracted increasing attention in recent years as a promising method for fabricating particle arrays in a controllable fashion, the two mentioned lithographic techniques fail to achieve selective allocation of particles into certain patterned regions. Currently, the concept of self-assembly has been frequently adopted for the nanostructuring of functional surfaces. To achieve both long-range order and high selectivity of regular particle arrays on patterned substrates, multiple-step hybrid approaches (using a top-down microfabrication approach combined with a subsequent bottom-up self-assembly process) are actively pursued.[8–10] Although these methods have been proven successful in producing patterned particle arrays, they are still fairly complicated and cannot be easily generalized. Up to now, reports of a one-step, versatile and robust method for the integration of regular nanoparticle arrays into micropatterned substrates are rather limited. In this study, we demonstrate a facile self-assembly method to fabricate rings of nanoparticle-decorated honeycomb-structured polymeric film through the combination of Pickering emulsions and capillary flow in the breath figures (BF) method.

The main basic methodology we have followed is the BF method. The BF method represents a single-step technique for fabricating films with ordered micrometer-size holes utilizing condensed water droplets as templates.[11] By casting polymer solution using volatile solvent under a flow of humid air, highly ordered honeycomb-patterned film can be formed. In a typical BF formation process, numberless water droplets floating on the surface of the solution are arranged into highly ordered arrays. Hence it introduces numberless patterned oil/water interfaces that can be utilized to control the assembly and alignment of materials with interfacial activities. As a bottom-up strategy, the BF method performs dynamic self-organization of the molecules having a self-assembling nature in nanometer scale. Amphiphilic materials have been widely used either as a single or second component of the casting solution to fabricate surfaces with chemically and topologically heterogeneous patterns. On the other hand, beginning with the original observations early in the 20th century, solid particles of colloidal size have been routinely employed to serve as stabilizers of emulsions, the so-called Pickering emulsions,[12] while in the past few years, people have reconsidered the possibilities of using fluid interface to control the assembly of nanoparticles. The number of publications concerning nanoparticle self-assembly at interfaces has been steadily increasing.[13–17] It is the attempt of this communication to direct silica nanoparticles onto BF microarrays in order to obtain certain hierarchical structuring of polymer and nanoparticles by self-organization processes at both micrometer and nanometer scale. The employment of the fluid directed self-assembly of nanoparticles at oil/water interfaces (Pickering

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emulsions) in the BF method is the very tool we used to achieve our goal. Interestingly, we found that capillary forces involved in the BF formation process also play an important role in the certain concentrated localization of the nanoparticles. The combination of Pickering emulsions and capillary flow in BF process would result in ring-like arrays of nanoparticles that are patterned within the ordered microporous films.

Experimental Section

Monodispersed silica nanoparticles (with mean diameters of 100 nm, 200 nm, and 1 μm) were prepared by hydrolysis of tetraethoxysilane (TEOS) in an alcohol medium in the presence of water and ammonia by the procedure originally described by Stöber et al.[18]

Fluorescence labeling of silica nanoparticles was performed via a modified Stöber method. It was a two-step process. In the first step, the fluorescent dye fluorescein isothiocyanate (FITC) was covalently attached to the silane coupling agent 3-aminopropyl triethoxysilane (APTES) by reacting the amine group of APTES with the thioisocyanate group of FITC. In the second step, the product of step 1 was added with other reactive components, just as in the preparation procedure of nonfluorescent silica particles.

In a typical honeycomb porous film preparation process, the casting solution was first obtained. The silica nanoparticles containing polymer solution was prepared by adding a few drops of silica nanoparticle suspension in absolute ethanol into polystyrene (PS) chloroform solution. The molecular weight of the PS we used is $M_w = 1.4 \times 10^5$. Then the polymer solution with or without nanoparticles was carefully introduced onto a clean glass substrate dropwise, and the substrate was placed under a stream of water-saturated air. The humidity of the air flow was maintained to be above 80%. After solidification, the film was dried at room temperature.

The fluorescence micrographs were taken with an Inverted fluorescence microscope (Olympus IX71). The excitation was set at 488 nm. Scanning electron microscopy (SEM) images were performed on a field-emission scanning electron microscope (FESEM; FEI, SiRion100). Optical images were taken under an Olympus BX-5 optical microscope (Tokyo, Japan) equipped with a digital camera.

Results and Discussion

Polymer solution with linear PS dissolved in chloroform was cast under humid conditions. In the case where we added no silica nanoparticles into the solution of PS, there were no ordered patterns formed on the film. This is in accordance with previous reports.[19,20] It may be explained that the linear PS without any polar substituents cannot effectively envelop the water droplets so that aggregation of droplets happens easily. After adding several drops of silica particle alcoholic suspension into the solution before casting, the obtained PS film shows honeycomb-patterned structure on the surface. Figure 1 shows SEM images of the morphological structure of the films prepared by a casting particle-containing solution. Highly ordered pores with silica particles selectively decorated within the interior walls of the open pores were formed (Figure 1a). A close examination of the film reveals that the particles preferentially assemble into the walls of the spherical cavities, and the flat ridges of pore intervals are very "clean". The self-organized arrays of micrometer-size holes extend over several square centimeters of substrate. In the certain regions where two pores are closely arranged, particles exhibit unusual gathering enrichment in pores (Figure 1b), which implied that nanopartilces will form a local dense coherent layer when two water droplets tend to coalesce. Such layers of nanoparticles
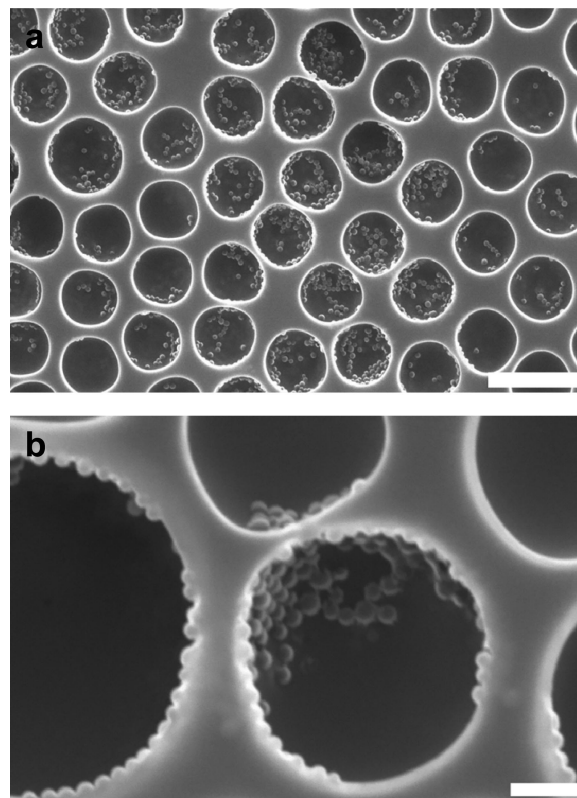

Figure 1. (a) SEM image of as-prepared silica nanoparticles (200 nm) aided BF arrays structure. (b) Magnified SEM image of structure as shown in panel a, showing gathering enrichment distribution of particles in the two neighboring pores. The scale bars are 5 μm (a) and 1 μm (b).

might act as a steric barrier against the contact and further coalescence of the templating water droplets.

So far several studies dealing with the fluid-directed self-assembly of nanoparticles in BF methods have been reported.[21−23] Nanoparticles have been proved to be able to serve as stabilizers of the templating water droplets in the BF formation process. Standard BF arrays can be obtained in the sole presence of particles because of the effective stabilization of water droplets by the self-assembly of nanoparticles at solvent/water interfaces, which is, in essence, the Pickering-emulsion effect.[21] The interfacial behavior of the colloidal particles has been described theoretically by Pieranski.[24] Once a single spherical colloidal particle that is initially suspended in a fluid adsorbs to the fluid interface, the energy E required to remove the particle from the interface is given by

$$E = \pi R^2 \gamma_{wo}(1 - |\cos \theta|)^2 \qquad (1)$$

where R refers to the particle radius, γ_{wo} represents the water/oil interfacial tension, and θ is the contact angle measured through the water phase.[13] For a given emulsion system (i.e., with fixed γ_{wo} and θ), the desorption energy, which is directly related to the stability of Pickering emulsions, depends on the particle size. When the particle is big enough, the value of E can be much

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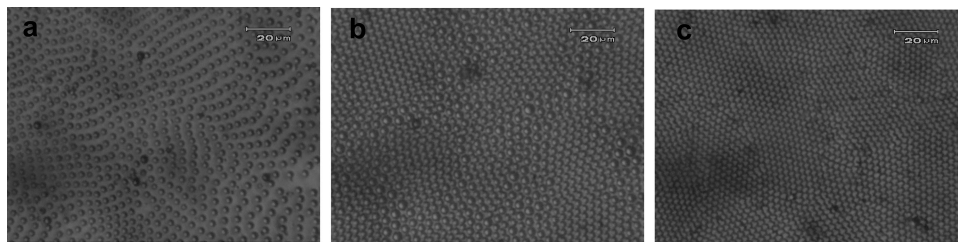(21) (a) Shah, P. S.; Sigman, M. B.; Stowell, C. A.; Lim, K. T.; Johnston, K. P.; Korgel, B. A. *Adv. Mater.* **2003**, *15*, 971. (b) Saunders, A. E.; Shah, P. S.; Sigman, M. B.; Hanrath, T., Jr.; Hwang, H.; Lim, K. T.; Johnston, K. P.; Korgel, B. A. *Nano Lett.* **2004**, *4*, 1943.
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Figure 2. Optical microscope images of films prepared from solutions containing particles with diameters of (a) 100 nm, (b) 200 nm, and (c) 1000 nm. All of the solutions were prepared by adding 30 μL of silica particle alcoholic suspension with a concentration of 10 mg/mL into 1 mL of PS chloroform solution with a concentration of 10 g L^{-1}.

larger than that of the thermal energy (a few k_BT), leading to an effective confinement of colloids to the interface. Hence, particles once held at the interface are much more stable than surfactant molecules that adsorb and desorb very fast. It makes colloidal particles better candidate materials than low molar mass surfactants to take advantage of the fluid interface-directed self-assembly. Pure nanoparticle systems applied in the BF method without any polymers have been investigated. For example, Korgel and his co-workers obtained ordered macroporous nanocrystal films using nanocrystals as a single casting component.[21] However, the possibility of fabricating regular nanoparticle arrays within a porous polymeric matrix under certain manipulation is also worth exploring.

To clarify the effect of particles on the geometry of the honeycomb structures, particles with different diameters were used to prepare the microporous films under identical conditions. As expected, with the increase of the particle size, the regularity as well as hole density of the corresponding film is significantly enhanced (Figure 2). The relatively larger size of nanoparticles with much higher desorption energy at the interface presents much better interfacial stabilizing performance. One can come to the same conclusion according to eq 1.

The interface-mediated assembly of the large particles surely has an impact on the "BF assembly" in microsize scale. The regional enrichment of particles in pores as shown in Figure 1b can be commonly seen within the film. This is similar to the experimental evidence of the "bridging" phenomenon recently described by Horozov and Binks.[25] They found that particles spontaneously accumulate in a dense layer, bridging the emulsion droplets sparsely covered with particles, while, in our case, particles compact into a "protective layer", which is believed to be helpful in stabilizing the water droplets.

It should be noted that, besides the hydrophilic silica particles we added, there is also ethanol in the solution, which is used to assist in the better dispersion of the particles. Serial experiments aiming to examine the possible influence of this water miscible solvent on the BF structure were carried out. Pure PS solution, the PS solution with added ethanol and the PS solution with added silica particle alcoholic suspension were respectively cast into films under the same casting conditions (see Supporting Information for micrographs of the entire series of films). Surprisingly, it turns out that the addition of ethanol, to some extent, facilitates the formation of the BF pattern in hydrophobic PS films. This may be explained according to the mechanism proposed by Li et al.[26] They succeeded in directly fabricating ordered porous poly(L-lactide) film using water-miscible tetrahydrofuran (THF) as solvent. They believed that THF would generate a certain diffusion region around the droplets because of the hydrophilicity of THF. Polymer in the solution underwent
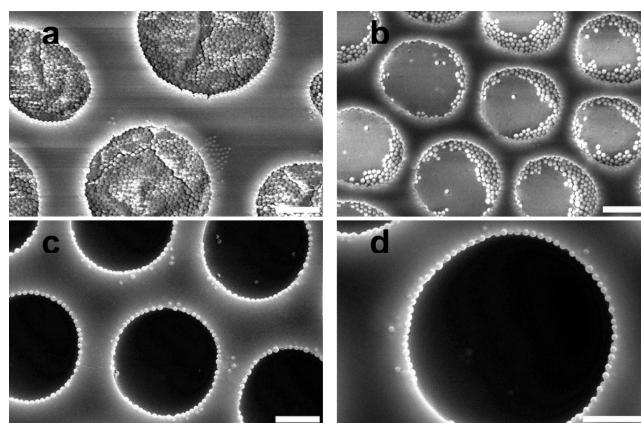
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Figure 3. (a−c) SEM images showing three representative patterned structures with different covering densities of decorating silica particles (200 nm). (d) Magnified SEM image of structure as shown in panel c, showing a single ring of nanoparticles. Films a−c were fabricated from solutions prepared by adding (a) 80 μL, (b) 50 μL, and (c) 30 μL of silica particle alcoholic suspension with a concentration of 10 mg/mL into 1 mL of PS chloroform solution with a concentration of 10 g L^{-1}. The scale bars are 2 μm.

conformational changes in the diffusion region and thus acted as a protective layer, which functioned well in stabilizing the water droplets. Ethanol is also able to serve as a "solvent surfactant", just like THF, while the addition of particles further enhanced the regularity of the BF structure. The addition of the silica particle alcoholic suspension may have a dual effect on the formation of BF arrays both from particles and ethanol.

The influence of the application quantity of silica nanoparticles on hierarchical micro- and nanostructuring was further investigated in our experiment. Interestingly, honeycomb-structured films with ordered micropores decorated by silica particles with different covering densities were formed by carefully controlling the experimental conditions (Figure 3a−c).

If one closely examines the allocation of the decorating particles within these hybrid structures, "particle rings", which consist of closely packed, well-ordered particle arrays, can be observed at the rims of the cavities. It is more prominent when a suitable amount of silica nanoparticles is used (Figure 3c,d). Figure 4a,b shows fluorescence images of such patterns by using FITC-labeled silica particles as probes. The hexagonal arrangement of fluorescent rings is in good agreement with the SEM images. It is well acknowledged that parameters of the BF arrays, such as pore size and pore intervals, can be conveniently manipulated by varying casting conditions. It makes easy control of these particle rings possible by applying this dynamic templating method. So it has an advantage over traditional ways of template-assisted self-assembly of spherical colloids in which the patterned arrays of particles are preset through the application of physical confinement.
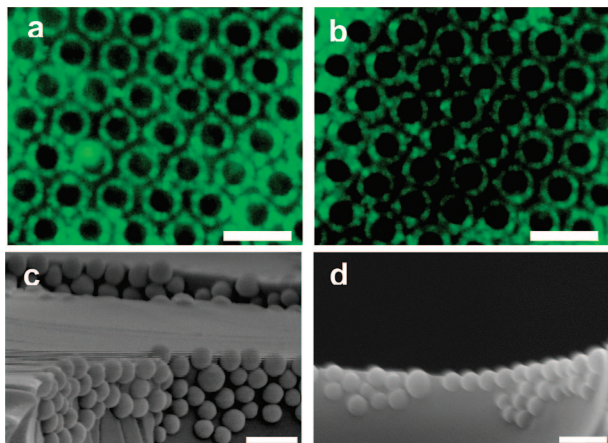
Figure 4. (a,b) Fluorescence images of ring-like patterns as shown in Figure 3c,d; FITC labeling silica nanoparticles (200 nm) were used as probes. (c,d) Cross-sectional SEM images of the structure shown in Figure 3c. The scale bars in a,b and c,d are 10 μm and 500 nm, respectively.
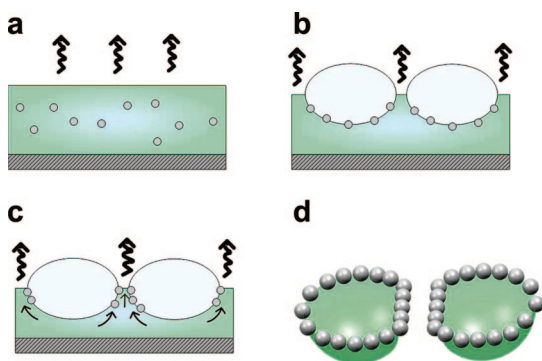

Figure 5. (a−d) A schematic representation of the formation of the rings of nanoparticles in BF arrays. See text for details.

Before discussing the possible mechanism of the rings of nanoparticle-decorated BF arrays, it is helpful to take account of capillary flow, a hydrodynamic self-assembly process, in the fluid-directed self-assembly of colloidal particles.[27] Deegan and his co-workers investigated the formation mechanism behind the ring-like pattern of particles formed from drying liquid suspension drops on a solid surface.[28] When the droplets dry on a surface with pinned contact area, an internal hydrodynamic capillary flow carries entrained particles to the air/liquid/substrate interface in which the ring-like pattern can be formed.[28] Here in our case, the formation of rings of nanoparticle-decorated BF arrays can be explained as the result of directed movement of nanoparticles under the cooperative action of Pickering emulsions and capillary flow.

Figure 5 presents a schematic representation of the formation of rings of nanoparticles in BF arrays. After the polymer solution containing silica particles is deposited onto the substrate, the organic solvent is allowed to evaporate under humid conditions, which leads to a condensation of numerous water droplets floating on the surface of the solution. Such a BF environment can be regarded as a water-in-oil emulsion system. The particles dispersed in solution spontaneously assemble into the interfaces of water/solution as a result of the Pickering emulsions effect in which a reduction in the interfacial energy is the dominant driving force (Figure 5b). Particles placed at the interfaces may further be transported into the three-phase contact line under the hydrodynamic drag forces, just like the case of drying suspension drops on a solid substrate.[28] The water in our case can be seen as the "substrate" since the evaporation rate of chloroform is much higher than water. After the growth of water droplets comes to its maximum equilibrium, chloroform is squeezed within the interstitials of the water droplets on the top surface of the solution. With the contact line pinning to its initial position, rapid evaporation of chloroform on the surface then induces a liquid flow from the interior (underneath the water droplets) to the contact line to compensate for evaporative losses. The capillary flow carries and further accumulates the particles to the region of the contact line, which is at the outer circumference of the droplet periphery. The particles are further compressed there by the liquid meniscus and form a fine ring-like array at the final stage of the BF process (Figure 5c,d). Solidification of the polymeric matrix eventually captures the particle rings. Cross-sectional SEM images of the obtained structures shown in Figure 4c,d provide clear proof of the migration and accumulation of particles to the three-phase contact line. So here, by the combination of Pickering emulsions and capillary flow, as well as the combination of thermodynamic and hydrodynamic self-assembly processes, in the BF method, we successfully achieve directed deposition of nanoparticle arrays within a patterned substrate.

Conclusions

In conclusion, we have demonstrated that the self-assembly of particles at the fluid/fluid interface (Pickering emulsions) can be well combined with the bottom-up technique of the BF method. Interestingly, when only a small number of nanoparticles were involved in BF process, they still tended to enrich at the air/solution/water interface as a result of the synergic action of Pickering emulsions and capillary flow. Rings of nanoparticle-decorated honeycomb-structured microarrays are formed via a one-step process. Such unique hierarchical structure with nanoparticles showing a high degree of organizational selectivity may have promising applications in the field of nanotechnology. It also opens an attractive route to produce materials with controlled physical structures at both the micrometer and nanometer scale via the combination of thermodynamic and hydrodynamic self-assembly.

Supporting Information Available: Optical microscope images of a series of films to examine the effect of ethanol and particles. This information is available free of charge via the Internet at http://pubs.acs.org.

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