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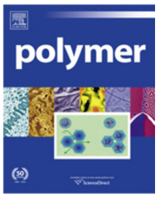

Particle-assisted fabrication of honeycomb-structured hybrid films via breath figures method

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Particle-assisted fabrication of honeycomb-structured hybrid films was carried out by employing particles as stabilizers in the breath figures (BF) method. Such a procedure tested the possibility of the combination of Pickering emulsions and breath figures, which are two classical self-assembly processes. Regularly patterned porous polystyrene film with particles decorating the inside walls of the open pores can be readily prepared. Silica particles were used as a model candidate to study the influence of both physical and chemical factors, including size, wettability, and application quantity, of the particles on BF pattern formation. Different assembling characteristics of the particles under different circumstances are also discussed. To further extend the application of such particle-assisted, bottom-up surface patterning technique to other kinds of particles, polystyrene particles and poly(N-isopropylacrylamide)-*co*-acrylic acid microgels were employed to serve as stabilizers in BF method. As expected, all three kinds of particles, including solid inorganic, solid polymeric and microgel ones, succeeded in assisting in the formation of BF arrays in polymer films. The introduction of Pickering-emulsion effect into BF method can provide new possibilities to develop particle-functionalized porous surface.

1. Introduction

Breath figures (BF) method is known as a fast-growing, bottom-up surface patterning technique to prepare micro-sized honeycomb-patterned porous films.[1–5] Such highly ordered microporous films could have potential applications in separation membranes,[6] photonic crystals,[7] catalysts,[8] electronics,[9] immobilization of biomolecules,[10] superhydrophobic surfaces,[11] and even light sensitive devices for astrophysics.[12] BF method is a special kind of patterning technique based on evaporation of polymer solutions.[13–15] It utilizes condensed water droplets as templates, which evaporate after they leave ordered imprints on the film surface.[5] The BF method is exceptionally simple and straightforward compared with other templating patterning techniques, which usually involve presetting and sacrificing of the templating materials.[16–21] Though the exact mechanism of BF method is now still under debate, it is commonly accepted that the crucial point for the formation of the BF arrays is the prevention of coalescence of water droplets.[22] Up to now, various materials have been used to prepare BF arrays including rod-coil block copolymers,[1] block copolymers,[23] amphiphilic copolymers,[24] star polymers.[4] All of these polymers are capable of effectively stabilizing the templating water droplets so that fine water droplets arrays can eventually lead to regular pattern formation on the polymer surface.

The term "breath figures" usually refers to the arrays of water droplets which can be formed when humid air comes into contact with cold solid or liquid surfaces.[25–28] For a typical BF procedure, after polymer solution using volatile solvent is cast under a flow of humid air, water droplets condense from humid environment due to the cooling of solution surface from the evaporation of the solvent, and arrange in a close-packing on the surface of the solvent. With arrays of water droplets floating on the surface of organic solvent, a special emulsion environment is created. The crucial point of the BF method, which is stabilization of the templating water droplets, can also be seen as stabilizing emulsions. From that point of view, it is quite understandable that amphiphilic materials have been widely used in the BF method. Though amphiphilic surfactants have been widely accepted as conventional emulsifier, it was recently shown that certain solid nanoparticles can also act as excellent emulsion stabilizers.[29–32] Back in the early stage of 20th century, solid particles of colloidal size have been routinely employed to serve as stabilizers of emulsions, the so-called Pickering emulsions.[33] Actually, there have been several attempts of using nanoparticles either as a single or second component of the casting solution to fabricate BF arrays.[34–36] Russell and his co-workers have reported a study of preparation of polymer BF film

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with quantum dot nanoparticles decorating the walls of the cavity.[37] This work utilized the spontaneous assembly of nanoparticles in the interface to achieve selective functionalization of micropatterned BF arrays. However, the particles were not used to assist in the preparation of the BF structure in their case. Neither did the Pickering-emulsion effect have been taken into account to further examine the possible effect the particles might have on the BF arrays. Recently, we introduced a procedure for fabricating delicate particle arrays within patterned substrate based on the particle-assisted BF method. [38] Considerably larger particles, compared with the particle size used in Russell's work, were used to achieve better Pickering-emulsion effect. Upon fine-tuning of the applied particles, circular rings of nanoparticle-decorated honeycomb-structured polymeric films can be obtained under synergistic action of Pickering emulsions and capillary flow.[38] In the current work, we carefully examined the particle-assisted BF method based on the combination of Pickering emulsion and BF method. The tuning of particle properties and the corresponding influence on the obtained BF structure gives direct insight of how these two self-assembly processes of BF method and Pickering emulsions can achieve synergistic effect. The influence of the variation of physical and chemical factors, including size, wettability, and application quantity, of the particles on the pattern morphology of the obtained polystyrene (PS) BF films was investigated. To further extend the application of such particle-assisted, bottom-up surface patterning technique to other kinds of particles, PS particles and poly(N-isopropylacrylamide) (PNIPAm)-*co*-acrylic acid (AA) microgels were employed to serve as stabilizers in the BF method. As expected, all three kinds of particles, including solid inorganic, solid polymeric and microgels, succeeded in assisting in the formation of BF arrays in polymer films.

2. Experimental section

2.1. Materials

Polystyrene (PS) (Mw = 1.4×10^5) was provided by Prof. Qiang Zheng. Monodispersed silica particles (with mean diameters of 100 nm, 200 nm, and 1 μm) were prepared by hydrolysis of tetraethoxysilane in an alcohol medium in the presence of water and ammonia by the procedure originally described by Stöber et al.[39] Hydrophobic silica particles were prepared by modifying silica surfaces using the silane coupling agent octadecyltrimethoxysilane (OTS), which has a hydrophobic octadecyl hydrocarbon chain. PS particles with ~200 nm diameters were purchased from Yiyi Nano (China). The PS particles were cross-linked so that they can be readily redispersed in organic solvent like chloroform. The PS particles were washed thoroughly with ethanol and deionized water by repeated centrifugation, and were collected by drying at 70 °C for 12 h before use. Poly(N-isopropylacrylamide) (PNIPAm)-*co*-acrylic acid (AA) microgels were prepared by precipitation polymerization.[40] NIPAm monomer (0.475 g), AA (0.024 g), and N,N-methylenebisacrylamide (0.052 g) dissolved in water (98 g) at room temperature were stirred at 400 rpm under N_2 for 30 min and then heated to 60 °C. After stabilizing the system at 60 °C for 15 min, polymerization was initiated by addition of potassium persulfate (0.060 g)/water (2 g) solution. The reaction was conducted under stirring at 60 °C for 4 h. The resultant microgel particles were dialyzed for 1 week against deionized water (twice daily changes of water) to remove surfactant and unreacted molecules. After dialysis, PNIPAm-*co*-AA microgels were concentrated by ultracentrifugation at 10 000 rpm for 1 h and redispersed in deionized water. The micogel particles were then collected by freeze dehydration for further redispersion in ethanol.

2.2. Film preparation

Before film preparation, casting solution was prepared by mixing PS chloroform solution with different particle suspensions. Linear PS was weighed in a sample vial and dissolved in chloroform to prepare polymer solutions with concentration of 10 g L^{-1}. Particles were dispersed either in ethanol or chloroform depending on their surface wettability properties for better mixing in the casting solution. Specifically, as-prepared hydrophilic silica particles and PNIPAm-*co*-AA microgel particles were dispersed in ethanol. Hydrophobic silica particles and PS particles were dispersed in chloroform. After adding certain particle suspension into polymer solutions, the casting solution was mixed ultrasonically. Quickly after the mixing, the casting solution was transferred onto a clean glass substrate dropwise. At the same time, a humidified flow of air was directed onto the liquid films on the substrate. After solidification, the obtained film was dried at room temperature.

2.3. Characterizations

The surfaces and cross sections of the microstructured films were characterized with a field-emission scanning electron microscope (FESEM; FEI, SiRion100), operating at a 25-kV accelerating voltage. Samples were made conductive by deposition of a gold layer in a vacuum chamber.

3. Results and discussion

3.1. The influence of silica particle size on the formation of ordered microporous films

Solid inorganic particles have proved to be employed to effectively serve as stabilizers for water-in-oil emulsions. While in the case of BF method, particles would spontaneously assemble into the interfaces of water/solution under the action of Pickering emulsions effect.[29] Physical and chemical properties of particles, which directly determine the ability of the particles to stabilize the emulsion would be naturally considered to have influences on the honeycomb structures prepared by the BF method.

Particle size is an important parameter to explore the effect of particles on the BF pattern formation. Silica particles with diameters of 100, 200 and 1000 nm were used to assist in preparing PS porous films by BF method. Fig. 1 shows the film surface morphology for each size of the particles. Particles with larger size clearly help to achieve better BF array preparation. 100 nm particles can barely make a regular honeycomb pattern. While, in the case of 1000 nm sized particles, films with perfect hexagonal arrangement of pores can be readily formed. According to the theory of Pickering emulsions, the size of particles predominantly determines the ability of the particles to stabilize emulsions. To be specific, the energy E which directly stands for the quantification index of the stabilization ability of the particles in Pickering emulsions is proportional to the square of the particle radius.[29] The energy E is given by:

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

where R stands for the particles radius, γ_{wo} represents the water/oil interfacial tension, and θ is the contact angle measured through the water phase. Under the condition that the values of γ_{wo} and θ are fixed (for a given emulsion system), E decreases markedly with reducing size since it depends on the square of the particle radius. Hence by using relatively larger particles, it is easier for one to prepare BF structures with good quality.

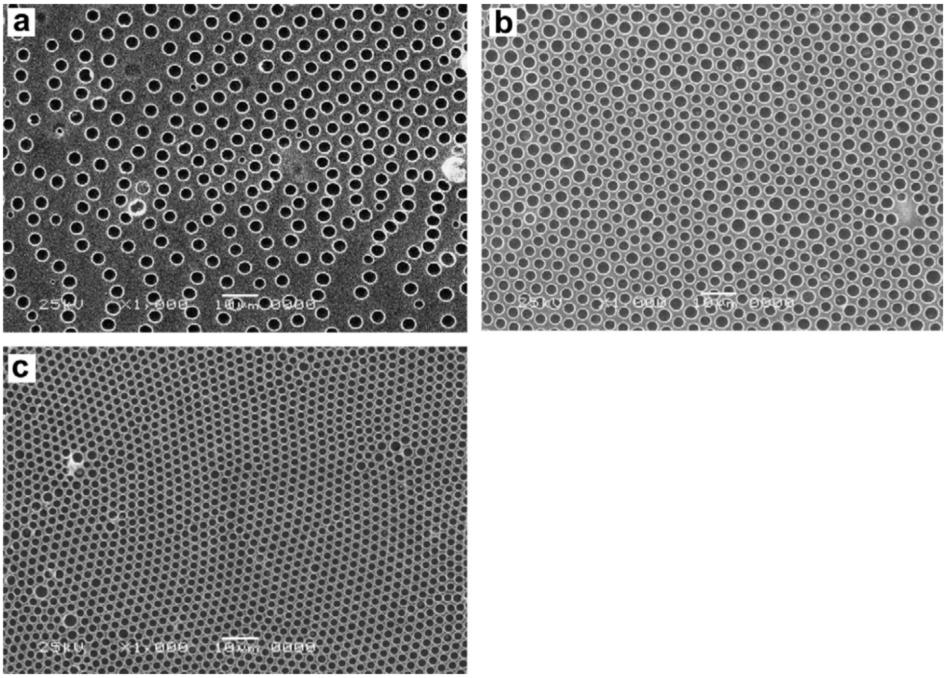

Fig. 1. SEM images of film fabricated from solutions prepared by adding 15 μL of silica particle alcoholic suspension (10 mg/mL) with particle diameters of 100 nm (a), 200 nm (b), 1000 nm (c), into 1 mL PS chloroform solution with concentration of 10 g L^{-1}. The scale bars are 10 μm (a–c).

In addition to investigate the "size" influence on BF arrays, it is also of interest to look into the assembling characteristics among particles with different size. We added equal quantities of two types of particles differing in size into the casting solution. Fig. 2 are the top and cross-sectional SEM images showing the assembling morphology of the hybrid particle mixing. Though theoretically the larger particles have better chances to assemble into the interfaces, there seems to be no obvious competitive preferential positioning onto the interior walls of the pores between these two kinds of particles. We assume that, on the condition of low particle surface coverage (Fig. 2c), preferential assembling of larger particles from solution into interfaces cannot result in preferential positioning onto the interior walls of the pores. Given enough time, the possible number advantage of large particles in the

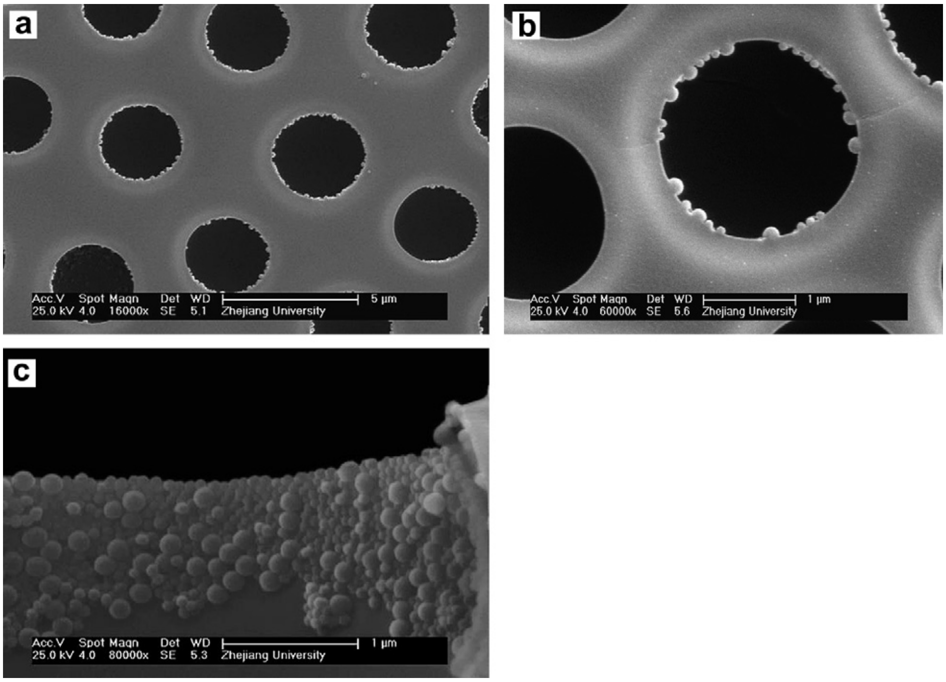

Fig. 2. (a,b) SEM images of film fabricated from solutions prepared by adding equal quantity of 100 nm mixed with 200 nm sized silica particle alcoholic suspension (15 μL each) with concentration of 10 mg/mL into 1 mL PS chloroform solution with concentration of 10 g L^{-1}. (c) Cross-sectional SEM images of the structure shown in Fig. 2 (a,b). The scale bars are 5 μm (a) and 1 μm (b,c).

interfaces will be offset. Both large and small particles can be seen on the rims of the relatively closed pores. Generally speaking, they spread evenly from the top edge of the pores down to the bottom. There is a slight distribution trend that the smaller particles occupy more of the higher positions than the larger ones. The larger size only has advantage in attaching to water droplets from solution. The vertical distribution of particles is rather dependent on the hydrodynamic capillary flow induced by the evaporation of the solvent. As we discussed in our previous study, once the particles are placed onto the interfaces, they will further be transported into the three-phase contact line under hydrodynamic drag forces.[38] The smaller particles are easier to be carried by capillary flow induced by solvent evaporation. Hence, it is understandable that the smaller particles have a better chance to be embedded higher in the pores than the larger ones.

3.2. The influence of wettability of silica particles on the formation of ordered microporous films

Wettability of particles is another important factor to be considered in Pickering emulsions. The wettability of particles in interfaces can be defined as the contact angle θ which a particle makes with the interface. For hydrophilic particles with $\theta < 90^\circ$, the particle surface resides more in water than in oil. While for hydrophobic particles with $\theta > 90^\circ$ the particle resides more in oil than in water.[29] According to equation (1), we can deduce that $E-\theta$ function curve is symmetrical with a single peak when θ is 90°. Same deviation of the value of θ from 90° would result in the same value of E. It means same extent of hydrophilicity and hydrophobicity will result in the same stabilization ability of the particles. To investigate the effect of the wettability of particles on the BF patterning procedure, both hydrophilic and hydrophobic silica particles were used to prepare BF structured films. It appears that a honeycomb-patterned structure could be successfully formed regardless of the wettability of the particles. Fig. 3a reveals that hydrophilic particles basically adsorb on the pore walls. It is evident that the hydrophilic nature of as-prepared silica particle makes them locate mainly in the water phase during the early stage of BF process. While in the case of hydrophobic particles (Fig. 3b,c), they show rather different assembly characteristics. The top SEM image (Fig. 3b) shows no trace of particles because the pore opening is relatively small. There are "roofs" over every pore covering larger cells underneath. Under the action of the interfacial tension between polymer solution and water droplets, precipitating polymer layers can be pulled around the droplet, creating a semi enclosed pore with an underneath "cell" and covering "roofs".[41] The cross-sectional SEM image (Fig. 3c) reveals that the hydrophobic particles are assembled into the interior walls of the pores hidden under the pore "roofs". Certain particles can be barely seen from the cavity walls with most parts residing in the polymer matrix since the hydrophobic particles only slightly immersed in the water phase. Hydrophilic particles show distinct assembling characteristics from hydrophobic ones due to different contact angles. The size of the pore openings is dependent on the interfacial tension between polymer solution and water droplets. With lower interfacial tension between polymer solution and water droplets, precipitating polymer layers cannot be pulled around the droplet, creating larger pore openings.[41] It is well acknowledged that droplet interfacial tension remains unchanged by particle adsorption at the interface in the case of Pickering emulsions.[42] Hence the large pore opening in the case of using hydrophilic particles must be attributed to the ethanol added with the particles. As discussed in our previous work, ethanol can function as a "solvent surfactant".[38] While, in the case of hydrophobic particles, the lack of ethanol makes the pore opening rather small.

3.3. The influence of application quantities of silica particles on the formation of ordered microporous films

In this part, by adjusting the amount of the particle suspension added into the casting PS chloroform solution, we tend to study the quantitative effect of particles adsorbing in the water/solution

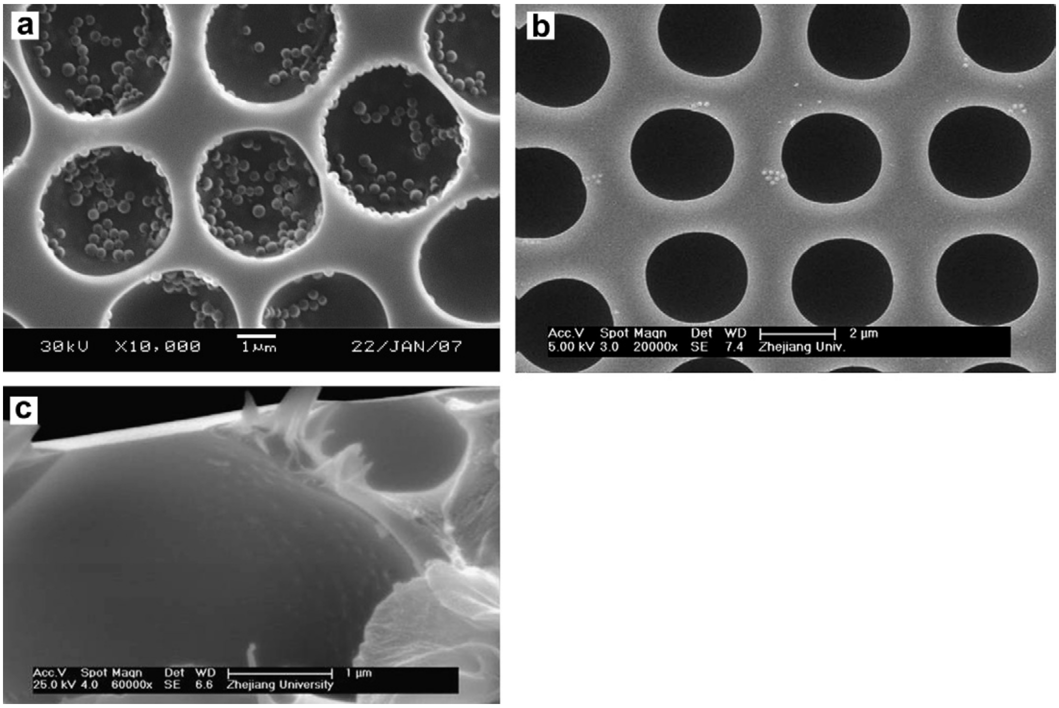

Fig. 3. (a,b) SEM images of film fabricated from solutions prepared by adding 30 μL of hydrophilic (a), hydrophobic (b), silica particle alcoholic suspension with concentration of 10 mg/mL into 1 mL PS chloroform solution with concentration of 10 g L^{-1}. (c) Cross-sectional SEM images of the structure shown in Fig. 3 b. The scale bars are 1 μm (a,c) and 2 μm (b).

interfaces which eventually become the interior walls of the pores. Fig. 4 are SEM images of PS films prepared by adding different quantities of silica particles. Different application quantities result in correspondingly different covering densities of particles decorating the patterned pores. It implies that particles added as a casting component can be actively involved into the self-assembly process of Pickering emulsions effect, resulting in the varying degrees of particle-decorating. It is known that particles placed at the interfaces would further act as mechanical barrier to prevent the templating water droplets from coalescencing.[38] That is how the addition of particles can facilitate the formation of the BF pattern on PS films. Under the condition of adding small amounts of particles (Fig. 4a,b), the particles show preferential accumulation into the edges of the cavities. Certain ring-like particle arrays (Fig. 4b) can be seen. That is the result of the combined action of Pickering emulsions and capillary flow.[38] When the quantity is further increased (Fig. 4c,d), particles can be seen as spreading densely from top to the bottom of the cavities. We note that rather small particle additions can facilitate good quality BF arrays on the surface of PS films. It has been reported that stable Pickering emulsions can be formed with low particle surface coverage as low as 5%.[42] It is not surprising to find that rather small particle additions in our case can facilitate good quality BF arrays on the surface of PS films.

As shown in Fig. 4, with increasing surface coverage within the pores, pore sizes become larger and pore intervals grow smaller. The shape of the pores is greatly altered from spherical to tessellated upon increasing particle adsorption. The regularity and uniformity have been compromised with large amount of particle addition. Particle adsorption onto the surface of the water droplets, due to the Pickering-emulsion effect, may retard evaporation rates from droplets. The more particles added, the more time the water droplets have to grow during BF formation process, creating bigger pores on the film surface. Longer growth time also makes the growing water droplets harder to be stabilized, leading to poorer regularity. On the other hand, liquid phase boundary tends to be deformed upon the adsorption of large amounts of particles.[43] With high particle covering density, water droplets cannot retain spherical forms, leaving the pores to display deformed shapes. If one closely looks into the morphology of BF arrays in Fig. 4, it can be seen that pore openings become larger with increased quantities of particles. The larger pore openings are caused by the gradual increasing quantity of ethanol, which reduces interfacial tension between polymer solution and water droplets (see relevant discussion in the second part of results of discussion).

3.4. Application of solid polymeric particles and microgels in the particle-assisted bottom-up surface patterning technique

In order to access the versatility of this particle-assisted, bottom-up surface patterning technique, we used solid polymeric particles and microgels as additional candidates other than inorganic particles to prepare BF patterned films. Figs. 5 and 6 describe the morphologies of the films obtained after using PS particles and PNIPAm-*co*-AA microgels as casting components respectively. Certain standard BF arrays can be readily obtained using both particles. The Pickering-emulsion effect can be well combined with BF method in the case of many kinds of particles including solid inorganic, solid polymeric and microgels. Though they have different mechanical properties, different surface wettability, different compatibility with polymer matrix, all three kinds of particles with similar sizes succeed in BF structure preparation as well as achieving selective assembly into particle arrays under the experimental conditions we have followed to prepare the films.

Though it works for all three kinds of particles in preparing particle-decorating well-fashioned porous films, the particle assembling structures are quite different from each other. It can be seen that PS particles merge well into the rim of the cavities, making a rolling borderline for the pore edge (Fig. 5a). And the PS particles located within the interior walls are better separately spreaded than silica particles. PS particles show larger spacing from each other and create a hexagonal configuration in localized regions (Fig. 5b–d). We assumed that the fine arrangement of PS particles is based on two reasons. On one hand, PS particles can

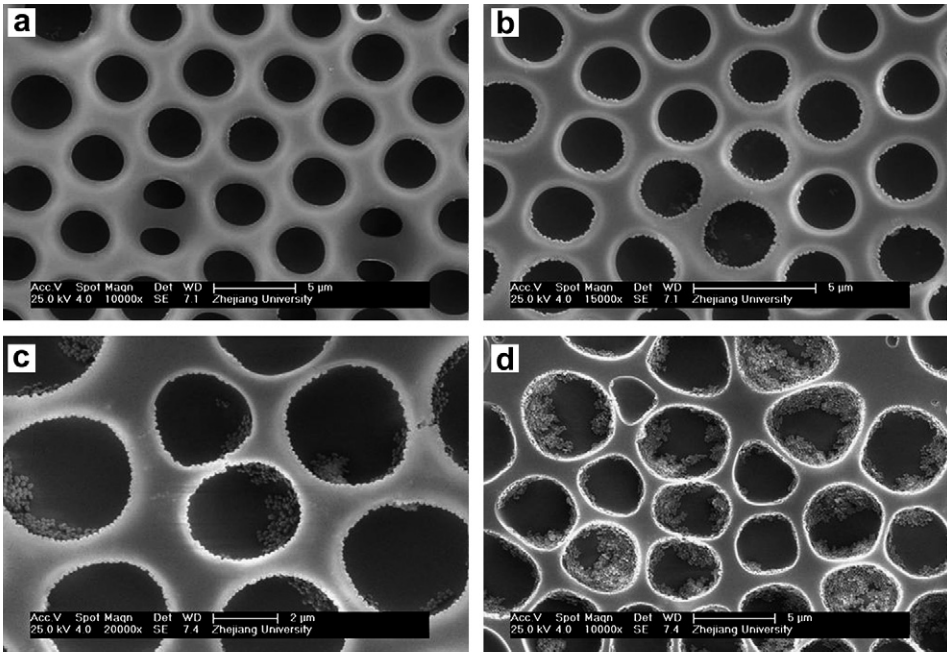

Fig. 4. SEM images of film fabricated from solutions prepared by adding 10 μL (a), 30 μL (b), 40 μL (c), 60 μL (d), silica particle alcoholic suspension with concentration of 10 mg/mL into 1 mL PS chloroform solution with concentration of 10 g L^{-1}. The scale bars are 5 μm (a,b,d) and 2 μm (c).

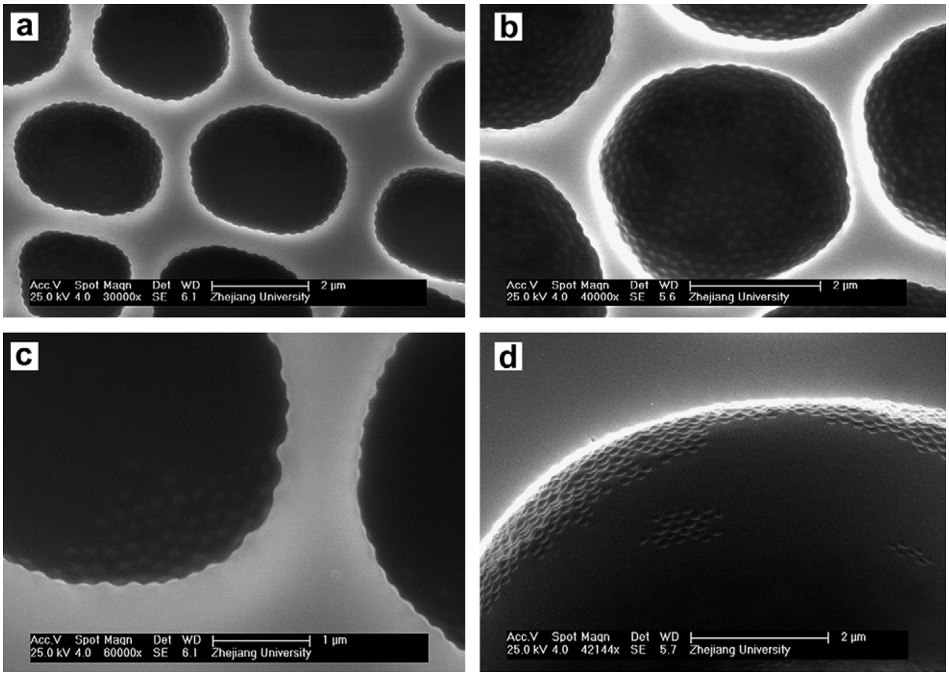

Fig. 5. SEM images of film fabricated from solutions prepared by adding 30 μL of PS particles alcoholic suspension with concentration of 10 mg/mL into 1 mL PS chloroform solution with concentration of 10 g L^{-1}. The scale bars are 2 μm (a,b,d), and 1 μm (c).

achieve better dispersion within PS solution than silica particles, so the assembling structures can be well optimized. When particles are placed on the liquid interfaces, interactive capillary forces, which are mediated by capillary bridges between two particles, will tend to organize the particles in a hexagonal lattice.[43] On the other hand, due to the good compatibility with polymer matrix, the arrays of PS particles at the interfaces can be well preserved during the solidification of the polymer matrix, and show no tendency of phase separation.

While in the case of PNIPAm-*co*-AA microgels, the dramatic difference in molecular chain flexibility and mechanical rigidity of particles between PNIPAm-*co*-AA microgels and conventional solid particles like silica or PS particles results in difficulties for assisting BF pattern preparation for microgels. Besides, microgels would go through a swelling process during the film preparation which is a liability in serving as stabilizers. So the regularity and homogeneity of the microgel-assisted BF patterns are not so optimal. Honeycomb-like porous structure decorated by microgels can be

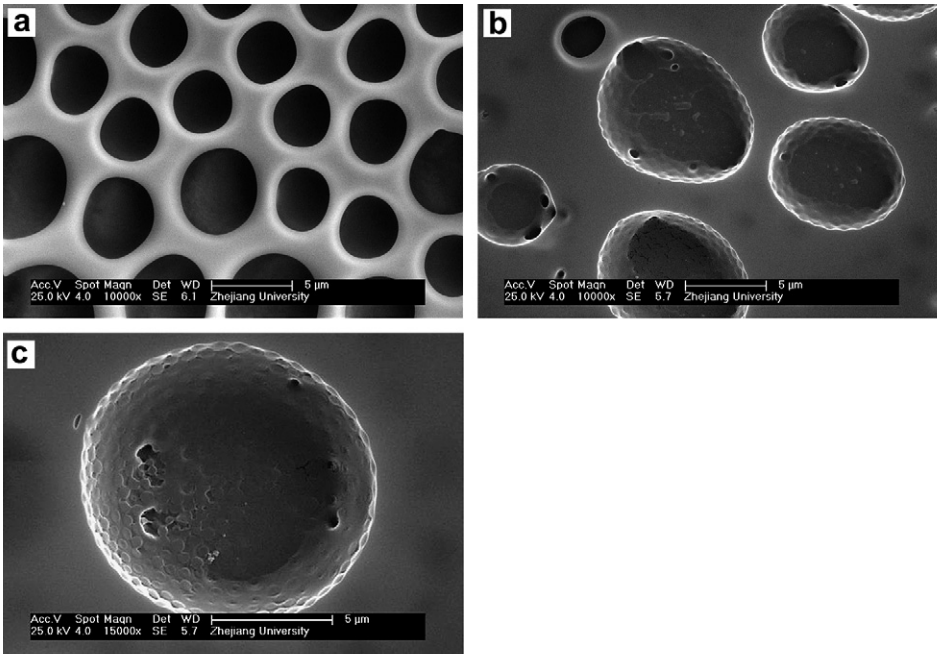

Fig. 6. SEM images of film fabricated from solutions prepared by adding 30 μL of PNIPAm-*co*-AA microgels alcoholic suspension with concentration of 10 mg/mL into 1 mL PS chloroform solution with concentration of 10 g L^{-1}. The scale bars are 5 μm.

formed under careful control of the experimental conditions (Fig. 6). As observed in Fig. 6c, flattened circular PNIPAm-*co*-AA microgels are well attached from the rim all the way to the bottom of the pores. Microgel arrays are produced with a fine hexagonal order. Overall, polymeric particles and microgels are successfully introduced as additives to facilitate the preparation of honeycomb-structured BF films. It is an inspiration for easy, functional modification of BF arrays.

4. Conclusions

This work has studied particle-assisted, bottom-up surface patterning technique which is based on the combination of BF method and Pickering emulsions. Silica particles of colloidal size were used as a model candidate to study the influence of both physical and chemical factors, including size, wettability, and application quantity, of the particles on BF pattern formation. Different assembling characteristics of particles under different circumstances are also discussed. Connections between BF method and Pickering emulsions have been discussed based on both BF array geometry and particle allocation. We also tested the possibilities of PS particles and PNIPAm-*co*-AA microgel particles in facilitating BF array preparation. And it has been proved that inorganic particles, polymeric particles and microgels can all be employed to serve as stabilizers in BF method. These results demonstrate a study in the novel particle-assisted, bottom-up surface patterning technique which may have great potential in producing functional porous structures. It also provides insight into BF and Pickering emulsions.

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