

Facilitated and Site-Specific Assembly of Functional Polystyrene Microspheres on Patterned Porous Films

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ABSTRACT Functional patterned materials have received considerable attention because of their potential applications in biochips, sensors, and optical or electronic materials. Here, we report a versatile approach to functional patterned films based on facilitated and site-specific assembly of microspheres. This method includes the hierarchical formation of honeycomb-patterned porous films from amphiphilic block copolymers and the assembly of functional polystyrene microspheres driven by the gravity and the electrostatic interaction. Polystyrene microspheres containing carboxyl groups with a narrow size distribution were synthesized by dispersion polymerization. Honeycomb-patterned porous films were prepared from polystyrene-*block*-poly(*N,N*-dimethylaminoethyl methacrylate) (PS-*b*-PDMAEMA) by the breath figure method and then quaternized. We found that direct deposition of the microspheres on the patterned films reaches high filling ratio only when using ethanol dispersions that can wet the film pores. Plasma treatment of the films improves the hydrophilicity and introduces charged species to the external surface as well as the pore surface, leading to nonspecific assembly of microspheres. Negatively charged microspheres dispersed in buffer solution show a facilitated and site-specific assembly on the quaternized film. The electrostatic interaction as well as the gravity facilitates the assembly and the suborder arrangement of the hydrophilic PDMAEMA block around the pores is responsible for the site-specific assembly. In addition, we demonstrate the applicability of this method in preparing photoluminescent patterns by the assembly of porphyrinated microspheres, which is useful in various fields such as intelligent sensing.

KEYWORDS: breath figure method • honeycomb-patterned film • microspheres • porphyrin • self-assembly • site-specificity

INTRODUCTION

The breath figure method, inspired by the foggy arrays of water droplets on cool solid surfaces, has received considerable attention for preparing honeycomb-patterned porous films (1). These films show great potential in advanced functional materials including separation membranes (2, 3), optical and electronic devices (4, 5), catalyst supports (6), templates (7–10), protein arrays (11–13), cell culture scaffolds (14–16), surface enhanced Raman scattering (SERS) substrates (17), microcontainers and microreactors (18), responsive materials (19, 20), and superhydrophobic surfaces (21–24). To fully satisfy the requirements of these interesting applications, researchers have developed various approaches to functional films. For example, thermally stable and solvent-resistant films were prepared by chemical or photochemical cross-linking (25–27). Metallic porous structures or organic–inorganic hybrid films were obtained via sol–gel process, chemical vapor deposition, electroless plating, metal ions binding, and self-assembly (28–31). Moreover, amphiphilic polymers (32–36), polymer blends (37–40), and polymers with functional end groups (11, 41) were used to fabricate films with functionalized pores. Microarrays such as protein arrays could be constructed by selective modification of such films through

immobilization of biomacromolecules (11, 12) and surface grafting by reversible addition–fragmentation chain transfer (RAFT) polymerization or atom transfer radical polymerization (ATRP) (42, 43).

Functional arrays with hierarchically ordered structures can also be effectively prepared using the patterned porous films as templates (44–55). Among them, assembly of microspheres on the films is quite interesting, which can be considered as a versatile approach to functional patterned films. Polystyrene (PS) microspheres show many features such as large specific surface area, high diffusibility and mobility, stable dispersions, high uniformity, and variety in surface chemistry and texture. They have been widely used in the fields of photonics, electronic and biotechnology (56). Shimomura and his colleges pioneered in the assembly of PS microspheres into the patterned porous films (54, 55). They pointed out that the PS patterned porous films are of hydrophobic surface and hence water dispersion of particles is not wet on them. Our results also confirmed that the PS porous films or even PS-based amphiphilic block copolymer films are hydrophobic (43). Therefore, Shimomura et al. treated the films using UV-ozone to improve the surface wettability and a specially designed instrument was used for the deposition of the microspheres.

In this work, we developed a direct, facilitated, and site-specific approach to the assembly of aqueous dispersions of functional PS microspheres on honeycomb-patterned porous films. We found that the electrostatic interaction as

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well as the gravity facilitates the assembly and the suborder arrangement of the hydrophilic block around the pores is responsible for the site-specific assembly. In addition, we demonstrate the applicability of this method in preparing photoluminescent patterns by the assembly of porphyrinated microspheres.

EXPERIMENTAL SECTION

Materials. Styrene (St) and acrylic acid (AA) were commercially obtained from Sinopharm Chemical Reagent Co. and distilled under reduced pressure before use. Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Iodomethane (CH_3I , 99%, Aladdin reagent Co. Ltd.) and poly(*N*-vinyl-2-pyrrolidone) (PVP-K30, Fluka) were used as received. Polystyrene-*block*-poly(*N,N*-dimethylaminoethyl methacrylate) (PS_{247} -*b*-PDMAEMA₁₄, $M_n = 27\,900$ g/mol, $MWD = 1.24$) was synthesized by ATRP using a reported procedure in tetrahydrofuran (THF) (57). Poly(ethylene terephthalate) (PET) film was kindly provided by Hangzhou Tape Factory and cleaned with acetone for 2 h before use. Water used in all experiments was deionized and ultrafiltrated to 18.2 $\text{M}\Omega$ with an ELGA LabWater system. All other reagents were analytical grade and used without further purification.

Characterization. Field-emission scanning electron microscope (FESEM, Sirion-100, FEI) was used to observe the surface morphology of films after being sputtered with gold using ion sputter JFC-1100. Fluorescence microscopy (CLSM) was performed on a Leica TCS SP5 confocal setup mounted on a Leica DMI 6000 CS inverted microscope (Leica Microsystems, Wetzlar) and was operated under the Leica Application Suite Advanced Fluorescence (LAS AF) program. Fluorescence spectrum of the film filled with porphyrinated microspheres was collected on Shimadzu RF-3510PC fluorescence spectrophotometer.

Synthesis of Polystyrene Microspheres. The synthesis was performed according to a slightly modified procedure (58). Briefly, the ingredients were weighed into a clean three necked bottle, bubbled with nitrogen, stirred slowly and then placed in a water bath kept at 70 °C for 24 h. The resultant dispersion was separated by centrifugation and washed with ethanol and water, and then dried under reduced pressure. For FESEM observation, the dispersion with a concentration of about 10 mg/mL in ethanol was prepared and dropped onto a piece of clean glass, which was then dried in air before FESEM observation. The FESEM images were analyzed with Image Pro Plus software. For each sample, more than 100 microspheres were measured to give the average diameter and the size distribution.

For the synthesis of porphyrinated microspheres, 0.2% (molar percent to styrene) of vinyl porphyrin monomer was additionally added. The vinyl porphyrin monomer, 5-(*p*-methacrylamidophenyl)-10,15,20-triphenylporphyrin, was synthesized according to our previously reported procedure (59).

Preparation and Quaternization of Patterned Porous Films. The films were cast by the breath figure method. Typically, an aliquot of 100 μL of carbon disulfide solution of PS-*b*-PDMAEMA was drop cast onto a PET film placed under a 1 L/min humid airflow. The humidity of the airflow was maintained to be above 80% by bubbling through distilled water and was measured by a hygro-thermograph (DT-321S, CEM Corporation). After solidification, the film was dried in air. For quaternization, the film was immersed in iodomethane/methanol solution (1% v/v) at room temperature for 2 h. Then, it was rinsed with methanol and dried at room temperature under reduced pressure.

Hydrophilization of the Patterned Porous Films. Dielectric barrier discharge plasma (Nanjing Suman Electronics Co. Ltd.) was utilized to improve the surface hydrophilicity of the films

Table 1. Synthesis of Functional Polystyrene Microspheres Containing Carboxyl Groups^a

sample	St (mL)	AA (μL)	AA/St	HA ^b (g)	$d \pm \text{SD}^c$
1	4.5	0	0	0.1650	1.18 ± 0.06
2	4.5	41	1%		1.58 ± 0.04
3	4.5	82	2%		1.62 ± 0.21
4	4.5	205	5%		1.32 ± 0.46^d

^a Typically, solvent ethanol is 35.5 mL, initiator AIBN is 41.2 mg, and stabilizer PVP is 0.5930 g. ^b Costabilizer hexadecanol, HA/St is 1.7% (molar ratio). ^c Average diameters of the microspheres and the size distributions. ^d Coagulum.

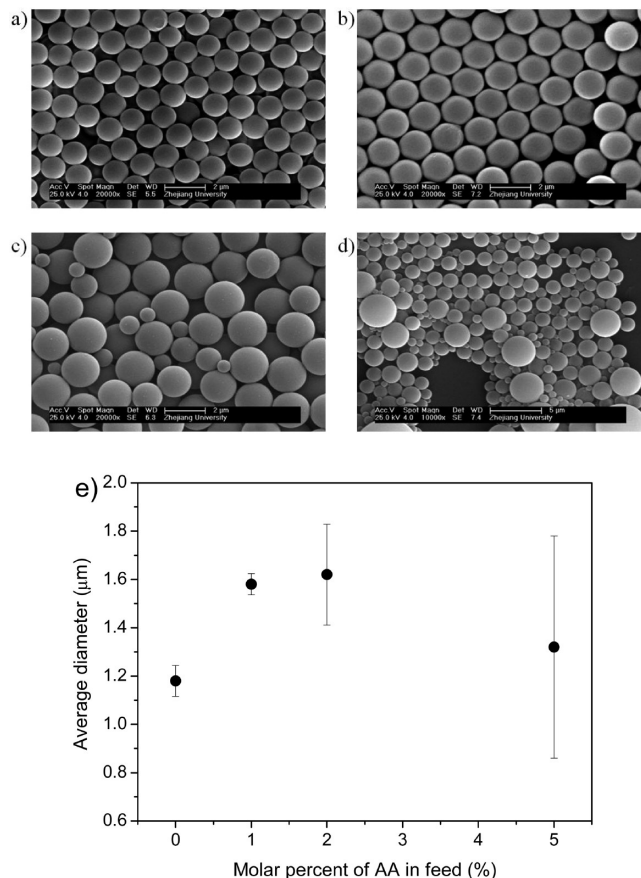


FIGURE 1. FESEM images of polystyrene microspheres containing carboxyl groups. Molar percent of AA in feed: (a) 0, (b) 1, (c) 2, and (d) 5%. (e) Diameters of the samples.

(60). Two quartz glass plates served as the dielectric layer. The argon (99%) at atmospheric pressure was used as the discharge gas. A piece of the film was put between the two parallel-plate electrodes with a gap of 2 mm, and irradiated at 10 kHz and 5 kV for 20 s. Subsequently, the treated film was washed with ethanol for 10 min and dried in air for further use.

Assembly of the Microspheres on the Patterned Porous Films. Microsphere dispersions in ethanol were prepared at a given concentration. The patterned porous film was then immersed into the dispersions for 5 min with gentle shaking. Afterward, the film was rinsed with ethanol to remove the microspheres adhered on the surface and dried in air. This process can be repeated several times. For the direct assembly of microspheres in aqueous dispersions, the solvent ethanol was replaced by phosphate buffer solution (PBS, pH 9.18).

RESULTS AND DISCUSSION

Synthesis of Functional Polystyrene Microspheres. Uniform polystyrene microspheres were prepared by dis-

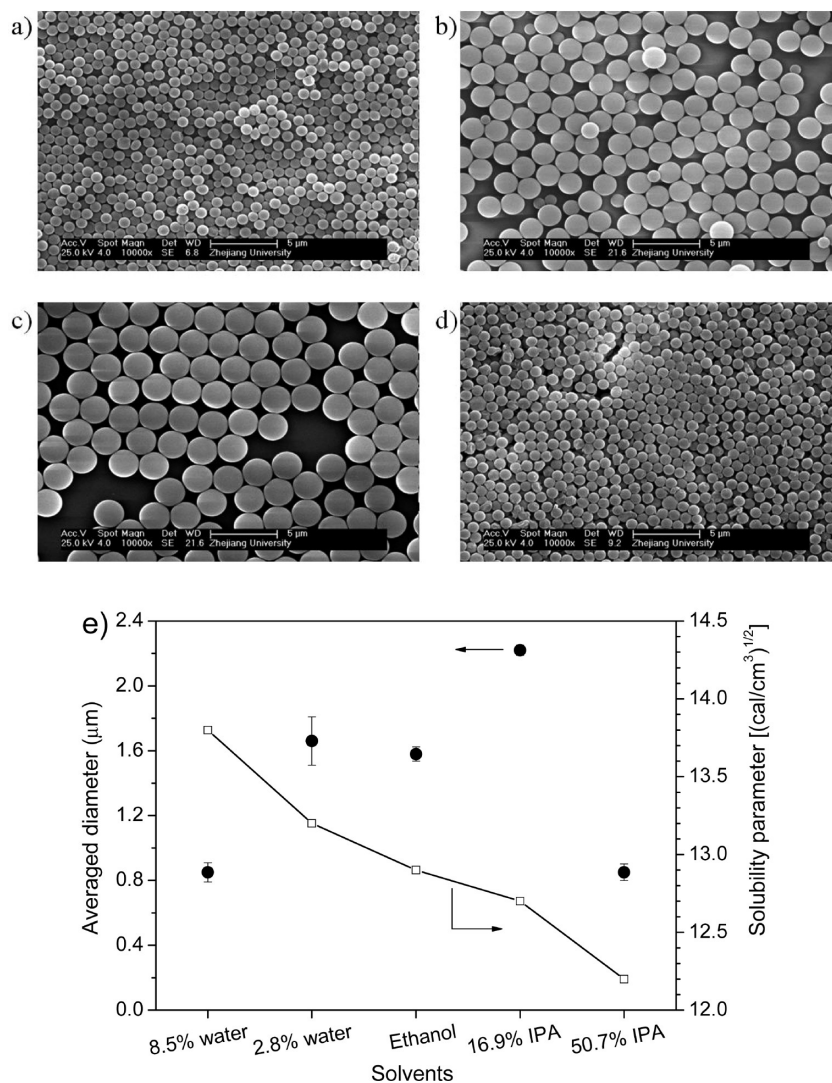


FIGURE 2. Using mixed solvents to modulate the diameters of polystyrene microspheres. Ethanol was mixed with the following solvents (volume percent): (a) 8.5% water; (b) 2.8% water; (c) 16.9% isopropanol; (d) 50.7% isopropanol. (e) Diameters of the samples.

persion polymerization, using AINB as initiator, PVP as stabilizer, and hexadecanol as costabilizer (Table 1). AA was used as a comonomer to introduce carboxyl groups into the microspheres, which displaced the costabilizer. As shown in Figure 1, the addition of 1% AA results in microspheres with uniform size. The average diameter increases from 1.18 to 1.58 μm compared with that using hexadecanol as the costabilizer. On one hand, it is due to the difference in the hydrophilicity of AA and hexadecanol. In the dispersion polymerization, the aggregative nucleation process may be controlled by the adsorption rate of the stabilizer and costabilizer. AA that is more hydrophilic has a slower rate of adsorption onto the precipitated hydrophobic PS oligomers. Thus the oligomers would tend to aggregate and form larger nuclei before enough stabilizer and costabilizer were adsorbed to stabilize them. On the other hand, copolymerization of St with hydrophilic AA may lead to a longer critical chain length and then a larger particle size. If the concentration of AA further increases to 5%, the microspheres have a broad size distribution and coagulum can be observed.

It is important to modulate the diameters of the microspheres in a range that is comparable to the pore diameters

of the honeycomb-patterned films. Microspheres with a narrow size distribution were prepared using mixed solvents (Figure 2). The average diameter of the microspheres decreases to about 0.8 μm by adding 8.5% water (volume ratio to ethanol, the same hereinafter) or 50.7% isopropanol. With 16.9% isopropanol in the mixed solvent, the microspheres have an average diameter of 2.2 μm . Note that the solubility parameters of water, ethanol, and isopropanol are 23.4, 12.9, and 11.5 $(\text{cal}/\text{cm}^3)^{1/2}$, respectively, it is speculated that the solubility of the oligomers in the mixed solvents with compatible solubility parameter increases the size of the resultant microspheres.

Preparation of Positively Charged Honeycomb-Patterned Films.

PS-*b*-PDMAEMA synthesized by ATRP was cast from CS_2 under a humid air flow to form patterned porous films. The pores show different sizes depending on the polymer concentration and they have a spherical cross profile (Figure 3). It has been elucidated that casting conditions such as polymer concentration have great effects on the morphology and the pore size of the cast films (43). In

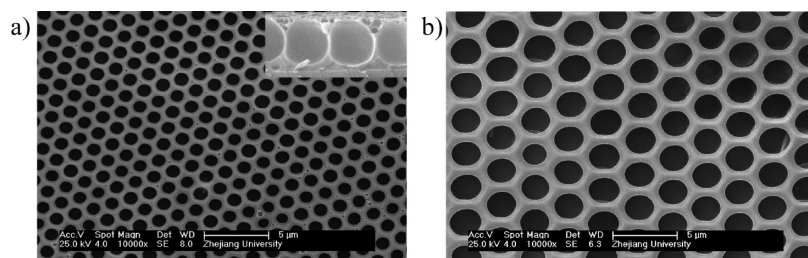


FIGURE 3. Honeycomb-patterned porous films prepared from PS-*b*-PDMAEMA solution with different concentrations: (a) 3 and (b) 1.5 mg/mL. Inset shows the cross-section of the film.

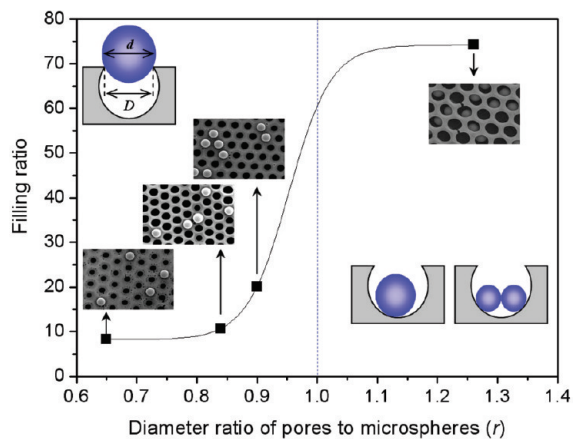


FIGURE 4. Effects of diameter ratio (r) of pores to microspheres on the filling ratio (f). Filling was performed 3 cycles for each sample with a dispersion concentration of 2.2 mg/mL.

this case, the average pore size increases from about 0.9 to 2.2 μm when the polymer concentration changes from 3 to 1.5 mg/mL.

The PDMAEMA block has a pK_a of 7.5, thus at pH below this value, the surface will be positively charged. However, quaternization is preferred in this work for creating a more stable positively charged surface. Another cause for quaternization is that the aqueous buffer cannot wet the pores, whereas the solvent for the quaternization (methanol) can, which ensures the subsequent assembly of microspheres driven by electrostatic interaction. Moreover, the quaternization process at solid–liquid interface is highly active in mild conditions. Detailed characterization of the positively charged films is discussed in our previous work (61). Results indicate that the quaternization ratio can reach about 80%. Also, there is no significant change in the topography before and after the quaternization in the iodomethane solution.

Filling of Microspheres Dispersed in Ethanol.

The simplest method to fill microspheres into the pores of the patterned films is direct deposition by the gravity. Microspheres dispersed in ethanol were used for the direct deposition. We investigated the effects of diameter ratios (r) of film pores (D) to microspheres (d) on the filling ratio (f , the ratio of the number of pores filled with microspheres to that unfilled). As shown in Figure 4, it is clear that when $r < 1$, the “filling” ratios are very low because the microspheres cannot come into the pores and are only supported by the rims of the pores. The increase in r lowers the centers of the gravity of the supported microspheres. Therefore, the microspheres become more stable and the “filling” ratio

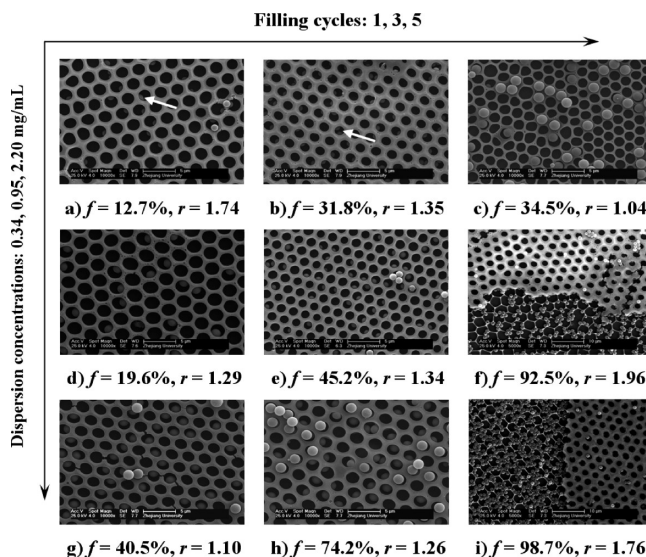


FIGURE 5. Effects of dispersion concentrations and filling cycles on the filling ratio (f) of microspheres on the honeycomb-patterned porous films. $r = D/d$, where D and d are the average diameters of film pores and microspheres, respectively. (f, i) Part of the film surface layer was removed using an adhesive tape after filling.

increases slowly. When r exceeds a critical value, the filling ratio increases sharply to more than 70% and will be only slightly influenced by the r value. In the following work, filling was therefore made under the condition of keeping $r > 1$.

Figure 5 shows the effects of dispersion concentrations and repeated filling cycles. High dispersion concentration or repeated deposition favors the filling, regardless of whether the diameter ratio increases or decreases ($r > 1$). Compared with multicycle deposition, high dispersion concentration seems to be more effective in promoting the filling. However, it is to be noted that very high dispersion concentrations can also lead to serious adsorption of the microspheres on the external surface of the patterned films, which cannot be removed by routine rinse (Figure 6).

Facilitated and Site-Specific Assembly of Microspheres from Aqueous Dispersions. As mentioned above, direct deposition of the ethanol dispersions of the microspheres can achieve very high filling ratios by the gravity. And the result of filling on quaternized films is the same (Figure 7a). However, some functional microspheres such as enzyme-immobilized ones are sensitive to organic solvents, hence in that case only aqueous dispersion can be used. Unfortunately, simple deposition does not work well with aqueous dispersion. On quaternized or unquaternized film, direct

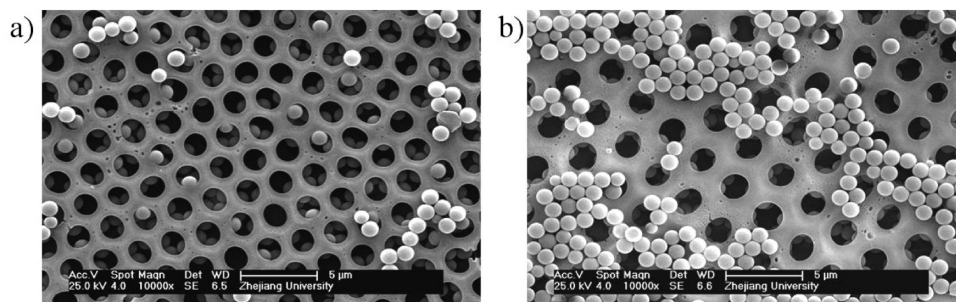


FIGURE 6. Filling of microspheres on the honeycomb-patterned porous films under high dispersion concentrations: (a) 4 and b) 6.7 mg/mL. The filling ratios (f) are more than 98%.

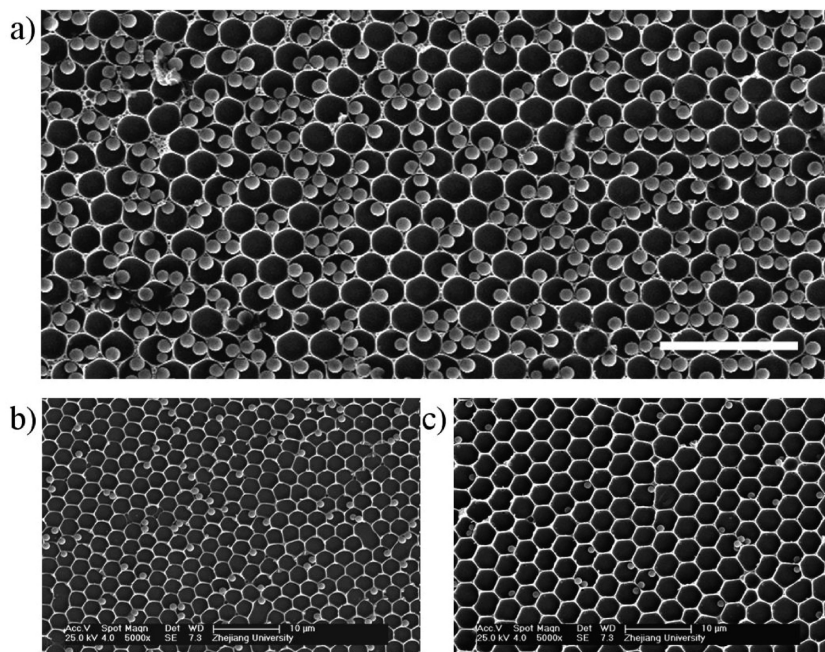


FIGURE 7. Filling of microspheres on the honeycomb-patterned porous films under different conditions: (a) ethanol dispersion on quaternized film, scale bar is 10 μm ; (b) aqueous dispersion on quaternized film; (c) aqueous dispersion on unquaternized film. The fillings were performed 5 cycles with a dispersion concentration of 2.2 mg/mL. The surface layers of the films were removed using an adhesive tape after the filling of microspheres.

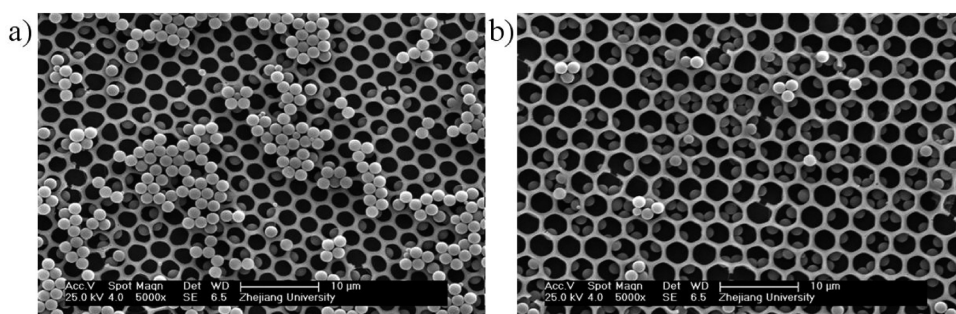


FIGURE 8. Filling of microspheres (a) on the honeycomb-patterned porous films treated by plasma, using aqueous dispersion ($f = 61.5\%$, $r = 1.38$); (b) on quaternized film using PBS dispersion (pH 6.8) ($f = 87.7\%$, $r = 1.72$). The fillings were performed 5 cycles with a dispersion concentration of 2.2 mg/mL.

deposition of the aqueous dispersions results in very low filling ratios, as confirmed by the micrographs of samples whose surface layers were peeled off using an adhesive tape after the filling of microspheres (Figure 7b,c).

To realize direct filling of the microspheres from aqueous dispersions, one common strategy is to treat the film to improve the surface hydrophilicity. The treatment by dielectric barrier discharge plasma at atmospheric pressure gener-

ates a hydrophilic surface, as indicated by the decrease of water contact angles (data not shown here). Another more straightforward proof is that experimentally white patterned porous films turn into semitransparent after being completely wetted with water. On one hand, a moderate filling ratio ($f = 61.5\%$) has been achieved on the treated film (Figure 8a). This filling may be due to not only the enhancement of surface hydrophilicity, but also the introduction of

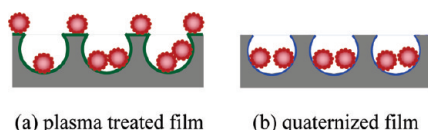


FIGURE 9. Illustration of the assembly of microspheres dispersed in aqueous solution. (a) Microspheres dispersed in deionized water assemble on the external surface as well as the pores of the plasma treated film. (b) Microspheres dispersed in PBS (pH 9.18) specifically assemble in the pores of the quaternized film.

charge species by the plasma treatment. It is well-known that plasma treatment can endow the surface, including the external surface as well as the pore surface, with some chargeable species such as amino groups and carboxyl groups. In other words, both positive charge and negative charge are introduced. As a result, the film surface was nonspecifically charged. Therefore, the resultant filling ratio increases but is not very high. On the other hand, similar to the direct deposition at very high dispersion concentration (Figure 6), many microspheres adsorb on the external surface of the film. It is reasonable if we keep in mind that the plasma treatment (or other similar treatments) is non-specific, which affects the external surface as well as the pore surface.

The microspheres containing carboxyl groups or protein-functionalized ones can be negatively charged by tuning the pH value. Assembly of the microspheres from PBS dispersions (pH 9.18) was performed on quaternized films. A high filling ratio ($f = 87.7\%$) has been realized (Figure 8b). Furthermore, the adsorption of microspheres on the external surface is negligible. In other words, it is a facilitated and site-specific assembly (Figure 9). This facilitated assembly is driven by the gravity and the electrostatic interaction. The site-specific assembly may be caused by the suborder arrangement of hydrophilic PDMAEMA block in the block copolymers. Our previous results and other studies have confirmed the aggregation of hydrophilic blocks or groups

in the pore walls during the film formation by the breath figure method (43). The aggregation may lead to uneven distribution of the positive charge by quaternization, i.e., positive charge mainly distributes inside the pores.

Utilization of the facilitated and site-specific assembly method may create various functional materials that are separated and patterned. For example, porphyrins and porphyrinated materials have found increasing applications in many areas such as molecular recognition or molecular imprinting, sensing, light-emitting and energy/electron transfer materials, and catalysis (59). Porphyrinated microspheres are well assembled into the honeycomb-patterned porous film (Figure 10a). As can be seen from the optical image, fluorescence image and their combined image (Figure 10b–d), photoluminescent patterns are obviously formed. Emission spectrum also confirms the assembly. This composite film with patterned porphyrinated microspheres may be useful in intelligent sensing.

CONCLUSIONS

An approach to facilitated and site-specific assembly of functional microspheres on honeycomb-patterned porous films has been developed. Direct deposition of the microspheres can reach high filling ratio only when using ethanol dispersions. Plasma-treated films lead to a nonspecific assembly of the microspheres dispersed in water because the external surface as well as the pore surface of the films is hydrophilized and charged. Direct assembly of the microspheres dispersed in phosphate buffer solution is very effective and site-specific. The facilitated assembly is driven by the gravity and the electrostatic interaction, and the specific assembly may be caused by the suborder arrangement of the hydrophilic PDMAEMA block around the pores. This versatile method is useful in construction of functional patterned materials such as photoluminescent patterns.

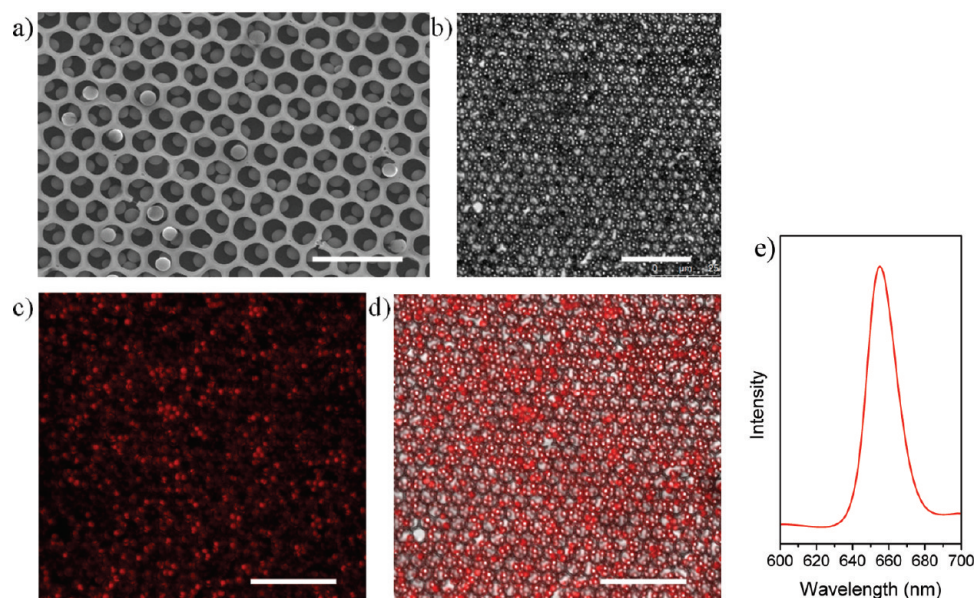


FIGURE 10. Filling of porphyrinated microspheres on the honeycomb-patterned porous film. (a) FESEM image; (b) optical image; (c) fluorescence image; (d) combined image of b and c; (e) fluorescence spectrum of the filled film excited at 420 nm. Scale bar: (a) 10 and (b–d) 25 μm .

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