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Fabrication of depth-controlled dimples on polymer microsphere and capturing of nano-sized objects

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ABSTRACT

Polymer microspheres containing submicron-sized surface dimples were prepared through the acid-dissolving removal of silica nanoparticles as templates from the surface of core-shell microspheres, which were prepared by modified suspension polymerization of a silica nanoparticle-dispersed polymerizable monomer mixture (methyl methacrylate and divinylbenzene dispersing). We demonstrated depth control of the dimples on the surface of polymer microspheres and evaluated their capturing properties. The depth of the dimples could be facilely controlled by changing the surface polarity of silica nanoparticles (1 μm) as templates during the synthesis of the core-shell microspheres. The depth of the prepared dimples ranged from 250 to 810 nm, and the gate diameter of the dimple was related to its depth owing to the spherical shape of the template. The inner surfaces of the dimples were evaluated based on the adsorption of cationic and anionic fluorescent dyes. Confocal laser microscopy observations indicated that the inner surfaces of the dimples were densely stained with both fluorescent dyes, whereas the outer surfaces of the microspheres were not stained, suggesting that the inner surfaces of the dimples were more hydrophilic. Silica particles smaller than the gate diameter of the dimple were crammed (or jammed) into the inner space of the dimple, and the captured silica particles did not drop off even after washing with water more than five times. Because the larger silica nanoparticles could not be trapped, the dimples could selectively capture the nanosized objects in their inner space.

KEYWORDS

Suspension polymerization; Core-shell microspheres; Hybrid particles; Self-assembly; Surface modification.

1. INTRODUCTION

The performance of polymer microspheres is strongly influenced by the morphology and characteristics of the surface. Hence, significant research has been conducted on controlling the surface microstructure. Various polymer microspheres with unique morphological surfaces, such as raspberry-like particles [1–4], rambutan-like particles [5], wrinkled particles [6–8], and dimpled particles [9–17], have been reported, for which specific methodologies have been applied to produce the desired surface morphology.

Spheres with dimple-shaped surfaces, such as golf balls, are of interest not only because they have a large specific area but also because they are water-repellent [18–20] and exhibit light-scattering [21–23] properties and frictional resistance in fluids [24]. The fabrication methods for the dimpled structure on the surface of polymer microspheres reported thus far can be divided into two groups: ones in which a template is used and ones in which the template is absent. For instance, methods in which the template is not used involve a phase separation of the polymers during seed emulsion polymerization [9–11] and removal of the template particles after electrostatically immobilizing them on a droplet surface [12,13]. In another study, an oil-in-water (o/w) emulsification technique combined with solvent evaporation was used to synthesize polymer particles to form dimpled structures on the surfaces of biodegradable polymers [14,15]. To improve the mono-dispersibility of polymer particles, dimpled particles were prepared by the photopolymerization of emulsions using the microfluidic method, followed by template removal [16,17].

To the best of our knowledge, there are few reports on controlling the depth of the dimples on the surface of polymer microspheres. In this study, we demonstrated the control of the dimple depth on the surface of polymer microspheres. We previously reported the preparation of polymer microspheres with unique surfaces via suspension polymerization using various inorganic nanoparticles [25–28]. Polymer microspheres with a wrinkled structure on the surface [25] and core-shell microspheres with silica nanoparticles regularly arranged on the surface [26,27] can be fabricated by changing the size and amount of silica nanoparticles added. Furthermore, hollow particles with hemispherical protrusions on the inner and outer surfaces [28] can be prepared using core-shell microspheres as templates through a sol–gel reaction of tetraethyl orthosilicate at the interface to form a silica shell layer, followed by calcination to remove the internal polymer.

In this study, core-shell microspheres with a silica nanoparticle shell layer were used to fabricate dimples by removing the surface-embedded silica nanoparticles from the core-shell polymer microspheres. The depth position of the embedded silica nanoparticles can be controlled by the surface hydrophilicity of the silica particles used as shell material for the core-shell polymer microspheres. The capture of the nanosized objects was evaluated using silica nanoparticles of different sizes. The inner surfaces of the dimples were characterized by dye molecule adsorption.

2. EXPERIMENTAL SECTION

2.1. Materials

Silica particles (S0.2 (MP-2040, d = 194 nm) and S1.0 (HIPRESICA FQ, d = 1.0 μm)) were purchased from Nissan Chemical Industries, Ltd. (Tokyo, Japan) and Ube Exsymo Co., Ltd. (Tokyo, Japan), respectively. 3-(Trimethoxysilyl)propyl methacrylate (M) was provided by JNC Co. (Tokyo, Japan). Methyltrimethoxysilane (C_1), propyltrimethoxysilane (C_3), and hexyltrimethoxysilane (C_6) were obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Styrene (S) and ethylene glycol dimethacrylate (E) were purchased from Fujifilm Wako Pure Chemical Corp. (Osaka, Japan) and used for copolymerization after removing p-tert-butylcatechol and hydroquinone inhibitors, respectively, with adsorbents. Benzoyl peroxide (BPO) was purchased from Nacalai Tesque, Inc. (Kyoto, Japan) and used as a thermal radical initiator after purification via recrystallization from chloroform/methanol. Poly(vinyl alcohol) PVA (MW = 1,500, 78%–82% deacetylated) was purchased from Fujifilm Wako Pure Chemical Corp. (Osaka, Japan) and used as an aqueous suspension medium. Hydrofluoric acid (48%) was purchased from Nacalai Tesque, Inc. (Kyoto, Japan) and was diluted to 4.8% before use for silica particle removal. Methyl orange and basic red were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), respectively, and used as fluorescent dyes for the adsorption experiments.

2.2. Preparation of dimpled polymer microspheres

The dimpled polymer microspheres were prepared in the following three steps. First, silica particles were dispersed in water by ultrasonic irradiation, 3-(Trimethoxysilyl)propyl methacrylate (M) in methanol solution was added, and then heated at 140 ℃ for 10 min in a microwave synthesis apparatus. After heating, the silica dispersion was washed with methanol, collected via filtration, and dried under vacuum. Second, the surface-modified silica particles were dispersed in a mixture of polymerizable monomers, namely styrene and ethylene glycol dimethacrylate, and benzoyl peroxide (BPO) was added as an initiator. The silica particle-dispersed monomer was poured into a 2 wt% polyvinyl alcohol (PVA) aqueous solution and stirred at 30 ℃ for 1 h. Thereafter, the temperature was increased to 80 ℃, and the suspension was stirred for 20 h.

Core-shell particles were collected by filtration after washing with methanol and hot water, and then dried under vacuum. Finally, dimpled polymer particles were obtained by immersing the core-shell particles in 4.8% hydrofluoric acid for 10 min to remove the template silica particles, followed by washing with water and methanol, filtration, and drying under vacuum.

2.3. Characterization of dimpled polymer microspheres

Surface modification of the silica particles was performed using a microwave chemical reaction apparatus (Monowave300, Anton Paar USA Inc., USA). After the modification, the functional groups on the silica particle surfaces were identified using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy (FT/IR-4100, JASCO Corporation, Japan). The organic components on the silica particle surfaces after the grafting of M were measured using a thermogravimetric analysis (TGA, TG/DTA6200, Seiko Instruments Inc., Chiba, Japan). The hydrophobicity of the silica particles was evaluated using an aqueous contact-angle meter (DM-501; Kyowa Interface Science Co., Ltd., Saitama, Japan). The size and surface morphology of the core-shell microspheres and dimpled polymer microspheres were characterized using optical microscopy (OM, CX31-P, Olympus Corp., Tokyo, Japan), scanning electron microscopy (SEM, JCM-5700, JEOL Ltd, Tokyo, Japan), and field-emission scanning electron microscopy (FE-SEM; SU-8000, Hitachi High-Tech Corp., Tokyo, Japan). The average particle diameter of the core-shell microspheres and the pore size of the dimples were statistically analyzed from the OM and SEM images using the A-Zoukun software (Asahi Kasei Engineering Corp., Kanagawa, Japan). The adsorption of the dye molecules onto the dimple spaces was evaluated using a UV–Vis spectrophotometer (V-560, JASCO Co., Tokyo, Japan) and confocal laser scanning microscopy (CLSM, TCS SP8, Leica Microsystems GmbH, Wetzlar, Germany).

3. RESULTS AND DISCUSSION

3.1. Preparation of dimpled polymer microspheres

Dimpled polymer microparticles were prepared by removing the template silica particles after the core-shell microparticles were prepared using modified suspension polymerization (Scheme 1). M-modified silica particles (*d* = 0.2 μm, MS0.2) were dispersed in a mixture of polymerizable monomers styrene (S) and ethylene glycol dimethacrylate (E) by sonication, and BPO was added as the initiator. Silica-dispersed monomer was poured into a 2 wt% PVA aqueous solution and stirred at a temperature of 30 ℃ for 1 h. Thereafter, the temperature was increased to 80 ℃, and the suspension was stirred for 20 h. The core-shell particles were collected by filtration after washing with methanol and hot water, and then dried under vacuum (MS0.2-5@pSE). The aqueous contact angles indicated that the hydrophobicity of the silica particles increased after modification with M (Fig. S1). The aqueous contact angles of the silica particles (S0.2 and S1.0) before surface modification were less than 10°. In comparison, they increased to 118° and 125°, respectively, after surface modification (MS0.2 and MS1.0). The silica particles before and after surface modification were dispersed in a mixture of toluene and water. Before modification, silica particles (S1.0) were dispersed in an aqueous phase, whereas silica particles after modification (MS0.2 and MS1.0) were dispersed in toluene (Fig. S2). These results indicate that the surface of the silica particles was hydrophobic. We confirmed that the silanol groups of silica remained intact after surface hydrophobization [25–

28]. Therefore, the interface of the silica particles became medium-polar even after hydrophobization, and silica particles self-assembled at the o/w interface during incubation, as shown in Scheme 1. Thereafter, the core-shell microspheres with a silica nanoparticle-layered shell could be obtained by polymerization. Table 1 summarizes the preparation conditions for the core-shell microspheres with different silica particle sizes and amounts, as well as the average particle diameters of the obtained microspheres. The average diameters of the core-shell microspheres with and without M-modified silica particles were largely the same, ranging from 36 to 47 μm. Fig. S3 shows the SEM images of the core-shell microspheres before the removal of the silica particles. In the core-shell microspheres containing 5 w/v% MS0.2 (MS0.2-5@pSE), silica particles were immobilized on the polymer surface at a high density (Fig. S3a). In contrast, core-shell particles containing 5 w/v% MS1.0 (MS1.0-5@pSE) had irregularly immobilized silica particles on the polymer surface, and some areas without silica particles were observed (Fig. S3b). This was probably due to the insufficient addition of silica to completely cover the polymer particles. The SEM observations of the surface of the core-shell microspheres prepared by increasing the amount of MS1.0 to 10 w/v% (MS1.0-10@pSE) showed that MS1.0 was arrayed and uniformly covered the polymer surface (Fig. S3c). Dimpled polymer particles were obtained by immersing the core-shell particles in 4.8% hydrofluoric acid for 10 min to remove the template silica particles, followed by washing with water and methanol, filtration, and drying under vacuum. Fig. 1 shows the SEM images of the dimpled particles (MS0.2-5@pSE and MS1.0-10@pSE) after silica removal. In all the cases, the silica particles of the template were completely removed, and a dimpled structure was observed on the polymer particle surface (Figs. 1a, 1b). Interestingly, the outlines of the dimples appeared to float (Fig. 1b). This may be because the silica particles were thinly covered by the monomer after self-assembly at the o/w interface during suspension polymerization. Therefore, the surface of the silica particles was still covered by a thin polymer layer after polymerization, and the HF treatment dissolved the silica from the top, which was considered to be the thinnest, so that the polymer film remained at the dimple periphery. The mechanism of the dimple structure formation is described below.

3.2. Control of the depth of dimple structure on the polymer surface

Dimpled polymer particles were prepared by varying the interfacial polarity of the silica particles to control the depth of the dimpled structure on the polymer particle surface. Three silane coupling agents with different alkyl chain lengths (C_1, C_3, and C_6) were used to control the interfacial polarity of the silica. The surface modification of S1.0 was performed in a manner similar to that employed for M. The amount of organic components grafted after surface modification was evaluated using a thermogravimetric analysis (TGA). The organic components of C_1S1.0, C_3S1.0, and C_6S1.0 were confirmed to be 0.75%, 0.75%, and 0.96%, respectively. The functional groups on the silica particle surfaces were evaluated using DRIFT-IR spectroscopy

(Fig. S4). The large peak near 1100 cm^{-1} is an absorption peak corresponding to the Si–O stretching vibrations of the silica particles. The absorption peaks corresponding to the C–H stretching vibrations of alkyl chains were identified at 2900 and 2950 cm^{-1} in C_1S1.0, C_3S1.0, and C_6S1.0 after surface modification. The aqueous contact angles were confirmed to increase with increasing alkyl chain length, up to 125°, 129°, and 134°, respectively (Fig. S5). The core-shell microspheres were prepared using silica particles with different degrees of hydrophobicity under the conditions listed in Table 1. The average diameters of the core-shell microspheres were 36.3, 41.7, and 47.3 µm, respectively. Fig. S6 shows the SEM images of the surface and cross-section of the core-shell particles before silica removal. The core-shell particles prepared with C_1S1.0 (C_1S1.0-10@pSE) showed that C_1S1.0 protruded considerably from the surface of the polymer particles and partially dropped off (Fig. S6a). The cross-sectional images also showed that C_1S1.0 is hardly embedded (Fig. S6b). This is attributed to the strong influence of the residual silanol groups on the silica surface; C_1 is considered hydrophilic even after surface treatment because of its short alkyl chains. Therefore, it is suggested that the silica particles self-assemble at the o/w interface during the incubation of suspension polymerization, and the force to move toward the aqueous phase is very strong, resulting in core-shell particles with almost no embedding. However, in the case of the core-shell particles prepared using C_3S1.0 (C_3S1.0-10@pSE) and C_6S1.0 (C_6S1.0-10@pSE), silica particles were observed to be embedded (Figs. S6c, S6e). In the cross-section of C_3S1.0-10@pSE, approximately half of the silica particles were embedded (Fig. S6d). In particular, the cross-sectional SEM images of C_6S1.0-10@pSE showed that the silica particles were deeply embedded at approximately 80% (Fig. S6f). The TGA results showed that the silica particle loadings within the core-shell particles were 6.9 wt% (C_1S1.0-10@pSE), 7.5 wt% (C_3S1.0-10@pSE), and 8.3 wt% (C6S1.0-10@pSE). It was confirmed that the silica particle loading increased with increasing alkyl chain length. Despite the addition of 10 w/v% silica particles during the preparation, C_1S1.0-10@pSE contained approximately 3 wt% less silica. This was probably due to the loss of some C_1S in the aqueous phase during suspension polymerization. The increase in the hydrophobicity of the silica particles with increasing number of alkyl chains makes it easier for the silica particles to remain in the monomer oil droplet. Therefore, the detachment of silica particles is considered to be more difficult. As the alkyl chains elongate, the interfacial polarity of the silica became more hydrophobic, which increased the contact area with the monomer oil droplet. As a result, it is expected to be more deeply embedded in the polymer particles. Fig. 2 shows the SEM images of the surface and cross-section of the dimpled polymer particles after immersion in HF for 1 h to remove the silica particles. The silica particles were completely removed from all the core-shell particles, forming dimpled structures on the polymer particle surfaces. The surface and cross-section of the polymer particles (C_1S1.0-10@pSE) prepared by removing C_1S from C_1S1.0-10@pSE, in which the silica particles were shallowly embedded, showed a shallow dimple structure (Figs. 2a, 2b). Furthermore, the shapes of the polymer particles were uneven. This was probably due to the hydrophilic interfacial polarity of silica, which allowed the polymerization to proceed without stabilization of the o/w droplets [29]. The polymer particles prepared by removing C_3S ($C_3S1.0$-10@pSE) and C_6S ($C_6S1.0$-10@pSE) were observed to have uniformly arranged dimpled structures on the polymer surface (Figs. 2c, 2e). Fig. 2d shows the cross-sectional SEM images of $C_3S1.0$-10@pSE. Approximately half of the silica particles were embedded. The cross-sectional SEM image of $C_6S1.0$-10@pSE shows that more than half of the silica particles were embedded (Fig. 2f). The aperture diameter of the dimple space on the surface of the polymer particles was measured using an image analysis software. Table 2 summarizes the depth of the dimple space calculated from the mean values of the aperture diameter and mean particle size of the silica particles. The average aperture diameter (d) and depth (D) were d = 0.87 μm, D = 0.25 μm ($C_1S1.0$-10@pSE), d = 0.92 μm, D = 0.69 μm ($C_3S1.0$-10@pSE) and d = 0.78 μm, and D = 0.81 μm ($C_6S1.0$-10@pSE), respectively. For $C_1S1.0$-10@pSE, only 25% of the silica particles were embedded, whereas for $C_6S1.0$-10@pSE, approximately 80% of the silica particles were embedded. These results indicate that changing the interfacial polarity of the silica particles can change the depth of embedment of the silica particles in the polymer particles and help control the depth of the dimple structure. As shown in Fig. 2e, for MS1.0-10@pSE, the contours of the dimpled structure float on the surface of $C_6S1.0$-10@pSE. A polymer film-like structure is also observed in these contours. A higher magnification image of the dimple structure showed a thin film of polymer that appeared to have been broken off (Fig. S7). To investigate the formation mechanism of the dimple structure, the immersion time of the silica particles in HF was varied using C_6S1.0-10@pSE to observe the dissolution of the silica particles. When the immersion time was 5 min, most of the silica particles remained undissolved. However, the silica particles protruding from the polymer surface were dissolved, and no protruding particles were identified. Some gaps were observed at the interface between the silica particles and polymer (Fig. 3a). When the immersion time was increased to 10 min, the silica particles became slightly smaller, and gaps were observed at the interface between the silica particles and the polymer in most dimples (Fig. 3b). When immersed in HF for 20 min, the dissolution of the silica particles progressed rapidly, and the silica particles were smaller than the aperture diameter of the dimple structure (Fig. 3c). One hour of immersion in HF confirmed that the silica particles completely disappeared from inside the dimpled structure (Fig. 3d). These results suggest that the silica particles on the surfaces of the polymer particles dissolved in the protruding portions. Subsequently, as the HF permeated the interface between the silica particles and the polymer, the silica particles dissolved gradually while maintaining their spherical shape. Finally, a dimple structure was formed.

3.3. Selective capturing ability of sub-micron space on the surface of polymer microspheres

A pod-like dimple structure with a small pore entrance and deep interior can selectively capture materials of specific sizes and hold them inside the dimple space. To investigate the behavior of solid material capture and retention inside the spaces of the dimple structures on the surface of the polymer particles, silica particles of different sizes were used as trapping materials. We mixed 10 mg of C_6S1.0-10@pSE with 1.0 g each of four different sized silica particles (0.2 µm, 0.5, 1.0, 2.0 µm) in powder form. After mixing with an Intelli-Mixer for 1 h, methanol was added, and the mixture was sonicated for 1 min. C_6S1.0-10@pSE was collected by filtration through a 5 µm mesh and dried under vacuum. Fig. 4 shows the SEM images of the surface of C_6S1.0-10@pSE after mixing and washing silica particles of various sizes. When silica particles (0.2 µm, 0.5 µm) with sizes smaller than the aperture diameter of the dimple structure (0.78 µm) were used, they were trapped inside the dimple pod space (Fig. 4a, 4b). Despite sonication for 1 min, silica particles could still be retained inside the dimple space. It is considered that the silica particles were densely packed inside the dimples and were therefore not easily released by physical vibrations. On the other hand, silica particles (1.0 µm, 2.0 µm) larger than the aperture diameter of the dimple structure (0.78 µm) were not captured into the dimple pod space (Figs. 4c, 4d). The selectivity of silica particle capture was also investigated by mixing 100 mg each of silica particles of different sizes (0.2, 0.5, and 1.0 µm) with 10 mg of MS1.0-

10@pSE and performing the same operation as described above. The SEM images showed that silica nanoparticles of 0.2 μm and 0.5 μm, which are smaller than the aperture diameter, were trapped inside the dimple space, whereas silica particles of larger sizes (1 μm) were not captured (Fig. 5). To investigate the nonphysical factors associated with the trapping and holding of silica particles inside the dimple space, two types of dye molecule adsorption experiments were conducted inside the dimple space. Dimple structures on the surface of the polymer particles were formed using silica particles as templates and removing them. Therefore, the inner surface of the dimple, where there was an interface with silica, and the outer surface of the dimple may have different chemical properties on the surface after removal of the silica particles. We added 100 mg of MS1.0-10@pSE to 5 mL of an aqueous solution of 0.1 mM methyl orange, and sonicated the mixture for 30 min under vacuum to introduce the dye solution inside the dimple space. After rapid washing with water, the dimples were immersed in water, and the elution of the dye was observed over time using UV–Vis spectroscopy. The same procedure was performed using basic red. When methyl orange was used, an absorption peak corresponding to methyl orange could be observed at 465 nm. An absorption peak was observed at the same wavelength in the post-immersion solution, indicating the elution of methyl orange (Fig. 6a). A secondary plot of the amounts of methyl orange eluted (Ab. at 465 nm) versus the immersion time confirmed that elution began immediately after immersion (0 min) and continued gradually until 30 min after immersion (Fig. 6b). When basic red was used, an absorption peak corresponding to basic red was observed at 525 nm. No absorption peaks corresponding to basic red were observed in the solution after immersion (Fig. 6c). The secondary plot of the basic red elution (Abs. at 525 nm) versus the immersion time showed no elution until after 10 min, and a slight elution was observed after 30 min (Fig. 6d). These results suggest that basic red was more easily adsorbed than methyl orange. As no elution was observed after 3 h of immersion in water, MS1.0-10@pSE was filtered, collected after 3 h, and observed under a confocal laser microscope. For both methyl orange and basic red, only the dimpled area emitted light, and no emission was observed on the outer surface of the dimple (Fig. 7). This indicated that the fluorescent dye was adsorbed only inside the dimples. MS1.0-10@pSE adsorbed methyl orange, which eluted more when immersed in water, and emitted a slightly weaker fluorescence (Fig. 7a). However, MS1.0-10@pSE adsorbed basic red, which showed almost no elution, and exhibited stronger emission (Fig. 7b). These results suggest that adsorption on the dimple inner surface was stronger for cationic basic red than for anionic methyl orange, indicating that the inner surface of the dimple was hydrophobic, though anionic groups were present.

4. CONCLUSIONS

Dimpled polymer particles were prepared using modified suspension polymerization to obtain core-shell particles, followed by the removal of silica particles as templates. Surface modification with silane coupling agents was found to be effective in controlling the interfacial polarity of the silica particles and stabilizing their self-assembly at the o/w interface during suspension polymerization. The dimpled structure on the polymer particle surface was precisely controlled using silica particles of different particle sizes and surface hydrophobicity. Using silica particles with strong hydrophobicity, we successfully fabricated a pod-like dimple structure with a narrow aperture and expanded interior space. The pod-like dimple structure could capture (storing) nanoparticles smaller than the aperture. It was possible to isolate submicron-sized spaces where diffusivity and fluidity exist from the external environment. Adsorption experiments conducted on the dye molecules inside the dimpled space showed that the inner surface of the pod was hydrophobic and anionic, and the fluorescent dye molecules were successfully captured (retained). These microspheres can be used as carriers or stationary phases to carry and transport substances stored inside the pod-like dimple space, and functional materials are expected to be developed using these features.

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REFERENCES

[1] M. Sadowska, Z. Adamczyk, M. Nattich-Rak, Formation of hematite nanoparticle monolayers of controlled coverage and structure at polymeric microparticles, J. Colloid Interface Sci. 505 (2017) 509-518, http://dx.doi.org/10.1016/j.jcis.2017.06.03.

[2] L. Wang, L. Y. Song, Z. Y. Chao, P. P. Chen, W. Y. Nie, Y.F Zhou, Role of surface functionality on the formation of raspberry-like polymer/silica composite particles: Weak acid–base interaction and steric effect, Appl. Sur. Sci. 342 (2015) 92-100, http://dx.doi.org/10.1016/j.apsusc.2015.03.042.

[3] H. Liu, D. Wang, X. Yang, Preparation of polymer@titania raspberry-like core-corona composite via heterocoagulated self-assembly based on hydrogen-bending nteraction, Coll. Surf. A 397 (2012), 48-58, https://doi.org/10.1016/j.colsurfa.2012.01.028.

[4] Z. Yuhong, Z. Qichao, S. Xingwang, T. Qingqiong, C. Min, W. Limin, Preparation of raspberry-like polymer/silica nanocomposite microspheres via emulsifier-free polymerization in water/acetone media, J. Colloid Interface Sci. 336 (2009) 544-550, https://doi.org/10.1016/j.jcis.2009.04.003.

[5] Y. Zhu, D. Hu, M. Wan, L. Jiang, Y. Wei, Conducting and superhydrophobic rambutan-like hollow spheres of polyaniline, Adv. Mater. 19 (2007) 2092-2096, https://doi.org/10.1002/adma.200602135.

[6] T. Zhao, D. Qiu, One-pot synthesis of highly folded microparticles by suspension polymerization, Langmuir 27 (2011) 12771-12774, https://doi.org/10.1021/la2028912.

[7] J. Yin, X. Han, Y. Cao, C. Lu, Surface wrinkling on polydimethylsiloxane microspheres via wet surface chemical oxidation, Sci. Rep. 4 (2014) 5710, https://doi.org/10.1038/srep05710.

[8] S. Liu, R. Deng, W. Li, J. Zhu, Polymer micropaticles with Controllable Surface Textures Generated through Interfacial Instabilities of Emulsion Droplets, Adv. Funct. Mater. 22 (2012) 1692-1697, https://doi.org/10.1002/adfm.201103018.

[9] M. Dai, L. Song, W. Nie, Y. Zhou, Golf ball-like particles fabricated by nonsolvent/solvent-induced phase separation method, J. Colloid Interface Sci. 391 (2013) 168-171, http://dx.doi.org/10.1016/j.jcis.2012.07.097.

[10] T. Fujibayashi, Y. Komatsu, N. Konishi, H. Yamori, M. Okubo, Effect of polymer polarity on the shape of “golf ball-like” particles prepared by seeded dispersion polymerization, Ind. Eng. Chem. Res. 47 (2008) 6445-6449, https://doi.org/10.1021/ie800188f.

[11] M. Okubo, Y. Murakami, T. Fujiwara, Formation mechanism of anomalous "golf ball-like" composite polymer particles by seeded emulsion polymerization, Colloid Polym. Sci. 274 (1996) 520-524, https://doi.org/10.1007/BF00655226.

[12] K. Watanabe, Y. Tajima, T. Shimura, H. Ishii, D. Nagao, Depletion-interaction-driven assembly of golf ball-like particles for development of colloidal macromolecules, J. Colloid Interface Sci. 534 (2019) 81-87, https://doi.org/10.1016/j.jcis.2018.08.117.

[13] K. Kadowaki, H. Ishii, D. Nagao, M. Konno, Imprinting dimples on narrowly dispersed polymeric spheres by heterocoagulation between hard polymer particles and soft oil droplets, Langmuir 32 (2016) 11600-11605, https://doi.org/10.1021/acs.langmuir.6b02688.

[14] G. Xi, W. Liu, M. Chen, Q. Li, X. Hao, M. Wang, X. Yang, Y. Feng, H. He, C. Shi, W. Li, Polysaccharide-based lotus seedpod surface-like porous microsphere with precise and controllable micromorphology for ultrarapid hemostasis, ACS Appl. Mater. Interfaces 11 (2019) 46558-46571, https://doi.org/10.1021/acsami.9b17543.

[15] M. R. Kim, S. Lee, J. Park, K. Y. Cho, Golf ball-shaped PLGA microparticles with internal pores fabricated by simple O/W emulsion, Chem. Commun. 46 (2010) 7433-7435, https://doi.org/10.1039/C0CC01738H.

[16] W. J. Duncanson, M. Zieringer, O. Wagner, J. N. Wilking, A. Abbaspourrad, R. Haag, D. A. Weitz, Microfluidic synthesis of monodisperse porous microspheres with size-tunable pores, Soft Matter 8 (2012) 10636-10640, https://doi.org/10.1039/C2SM25694K.

[17] S. H. Kim, J. W. Shim, J. M. Lim, S. Y. Lee, S. M. Yang, Microfluidic fabrication of microparticles with structural complexity using photocurable emulsion droplets, New J. Phys. 11 (2009) 075014, DOI: 10.1088/1367-2630/11/7/075014.

[18] K. H. Hwangbo, M. R. Kim, C. S. Lee, K. Y. Cho, Facile fabrication of uniform golf-ball-shaped microparticles from various polymers, Soft Matter 7 (2011) 10874-10878, DOI https://doi.org/10.1039/C1SM06529G.

[19] J. Seo, S. K. Lee, J. Lee, J. S. Lee, H. Kwon, S. W. Cho, J. H. Ahn, T. Lee, Path-programmable water droplet manipulations on an adhesion controlled superhydrophobic surface, Sci. Rep. 5 (2015) 12326, https://doi.org/10.1038/srep12326.

[20] I. You, T. G. Lee, Y. S. Nam, H. Lee, Fabrication of a micro-omnifluidic device by omniphilic/omniphobic patterning on nanostructured surfaces, ACS Nano 8 (2014) 9016-9024, https://doi.org/10.1021/nn502226v.

[21] J. Mo, X. Chang, D. Renqing, J. Zhang, L. Liao, S. Luo, Design, fabrication, and performance evaluation of a concave lens array on an aspheric curved surface, Opt. Express 30 (2022) 33241-33258, https://doi.org/10.1364/OE.471055.

[22] L. Mei, C. Qu, Z. Xu, G. Wang, J. Zhang, X. Guo, Y. Peng, Facile fabrication of microlens array on encapsulation layer for enhancing angular color uniformity of color-mixed light-emitting diodes, Opt. Laser Technol. 142 (2021) 107227, https://doi.org/10.1016/j.optlastec.2021.107227.

[23] X. Ding, J. Li, Q. Chen, Y. Tang, Z. Li, B. Yu, Improving LED CCT uniformity using micropatterned films optimized by combining ray tracing and FDTD methods, Opt. Express 23 (2015) A180-A190, https://doi.org/10.1364/OE.23.00A180.

[24] J. Li, M. Tsubokura, M. Tsunoda, Numerical Investigation of the Flow Past a Rotating Golf Ball and Its Comparison with a Rotating Smooth Sphere,Flow Turbul. Combust. 99 (2017) 837-864. https://doi.org/10.1007/s10494-017-9859-1

[25] N. Hano, M. Takafuji, H. Ihara, One-pot preparation of polymer microspheres having wrinkled hard surfaces through self-assembly of silica nanoparticles, Chem. Commun. 53 (2017) 9147-9150. https://doi.org/10.1039/C7CC05132H

[26] N. Hano, N. Ryu, S. Nagaoka, H. Ihara, M. Takafuji, Selective reflection enhancement by controlling of surface-layering structure of inorganic

nanoparticles on polymer microspheres, Coll. Surf. A 637 (2022) 128188. https://doi.org/10.1016/j.colsurfa.2021.128188

[27] H. Ihara, S. Kubota, A. Uchimura, Y. Sakai, T. Wakiya, M. M. Rahman, S. Nagaoka, M. Takafuji, A facile preparation method for self-assembled monolayers with silica particles on polystyrene-based microspheres, Mater. Chem. Phys. 114 (2009) 1-5. https://doi.org/10.1016/j.matchemphys.2008.09.043

[28] M. Takafuji, N. Hano, Md. A. Alam, H. Ihara, Fabrication of hollow silica microspheres with orderly hemispherical protrusions and capability for heat-induced controlled cracking, Langmuir 33 (2017) 10679-10689. https://doi.org/10.1021/acs.langmuir.7b02223

[29] B. P. Binks, Particles as surfactants-similarities and differences, Curr. Opin. Colloid Interface Sci. 7 (2002) 21-41, https://doi.org/10.1016/S1359-0294(02)00008-0.

Table 1

Table 1 Preparation conditions[a] and characterization of core-shell microspheres

Microsphere	St/EGDMA (mL/mL)	Silica particles		2 wt% PVA aq. (mL)	BPO (g)	Obtained microsphere
		Name	Amount (g (w/v%))			Average particle diameter[b] (μm)
pSE	7.5/7.5	–	0 (0)	300	0.15	36.0
MS0.2-5@pSE	7.5/7.5	MS0.2	0.75 (5)	300	0.15	44.7
MS1.0-5@pSE	7.5/7.5	MS1.0	0.75 (5)	300	0.15	36.2
MS1.0-10@pSE	7.5/7.5	MS1.0	1.50 (10)	300	0.15	38.4
C_1S1.0-10@pSE	3.75/3.75	C_1S1.0	0.75 (10)	250	0.125	36.3
C_3S1.0-10@pSE	3.75/3.75	C_3S1.0	0.75 (10)	250	0.125	41.7
C_6S1.0-10@pSE	3.75/3.75	C_6S1.0	0.75 (10)	250	0.125	47.3

[a] Core-shell microspheres were prepared by pre-stirring at 30 ℃ for 1 h and performing suspension polymerization at 80 ℃ for 20 h.

[b] The average particle diameter was statistically analyzed from the OM or SEM images using the A-Zoukun software (Asahi Kasei Engineering Corporation, Japan).

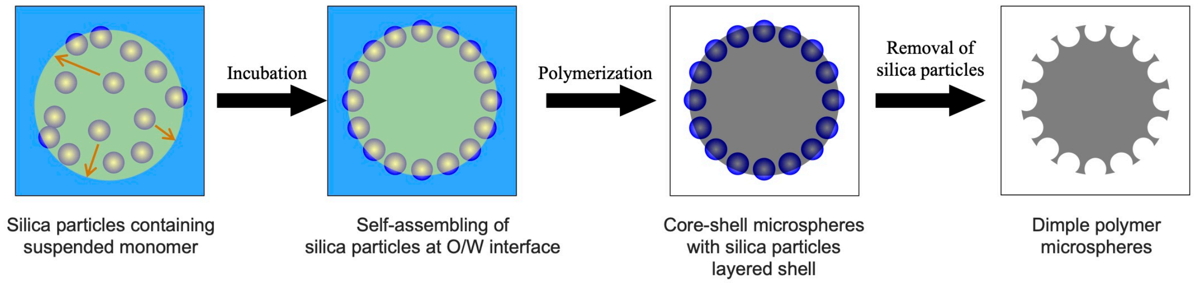
Table 2

Table 2 Summary of the depth of dimple space on the surface of polymer particles

Microsphere	Dimple space	
	Aperture diameter[a] (d) (μm)	Depth (D) (μm)
C_1S1.0-10@pSE	0.87	0.25
C_3S1.0-10@pSE	0.92	0.69
C_6S1.0-10@pSE	0.78	0.81

[a] The average aperture diameter was statistically analyzed from the SEM images using the A-Zoukun software (Asahi Kasei Engineering Corporation, Japan).

Scheme 1



Scheme 1. Schematic of the preparation of dimpled polymer particles.

Figure 1

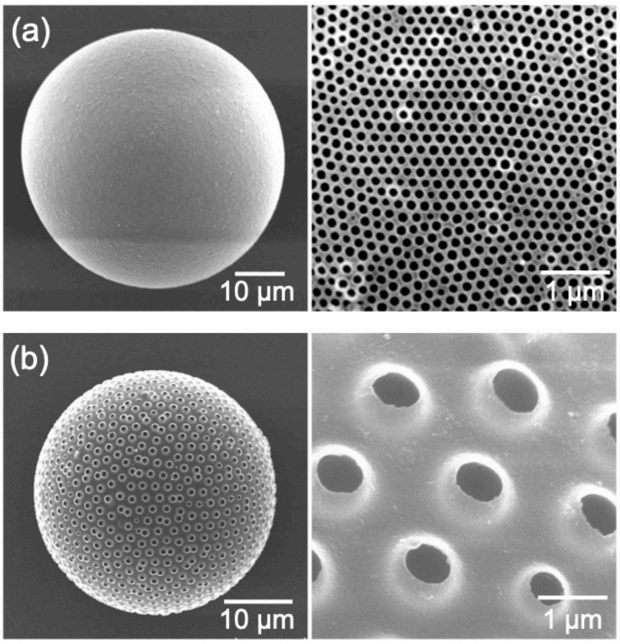


Figure 1. SEM images of dimpled polymer particles prepared with different sizes of silica particles: a) 0.2 µm, and b) 1.0 µm.

Figure 2

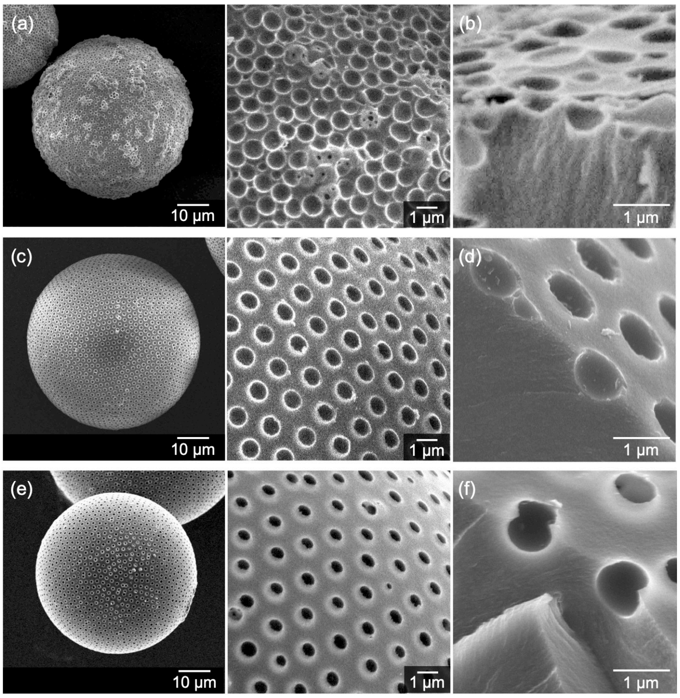


Figure 2. SEM images of surface and cross-section of dimpled polymer particles prepared with silica particles having various surface polarities: a) $C_1S1.0$, b) $C_3S1.0$, and c) $C_6S1.0$.

Figure 3

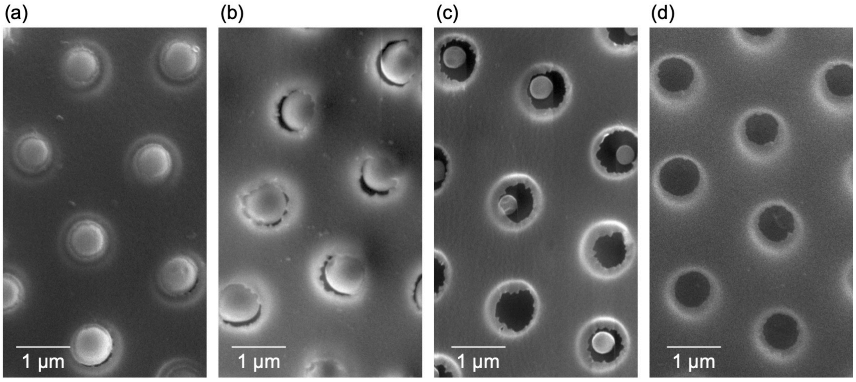


Figure 3. SEM images of $C_6S1.0$-10@pSE with respect to the time of immersion in HF: a) 5 min, b) 10 min, c) 20 min, and d) 60 min.

Figure 4

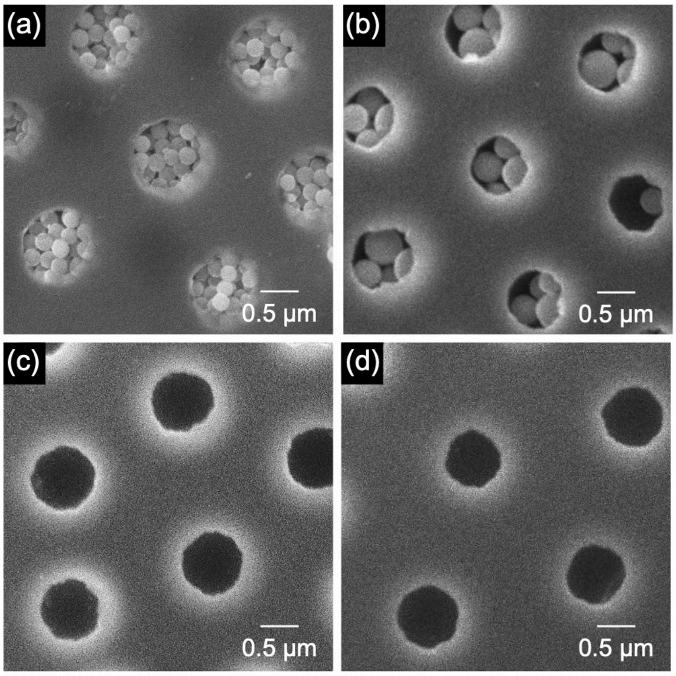


Figure 4. SEM images of the surface of $C_6S1.0$-10@pSE after mixing and washing silica particles of various sizes: a) 0.2 µm, b) 0.5 µm, c) 1.0 µm, and d) 2.0 µm.

Figure 5

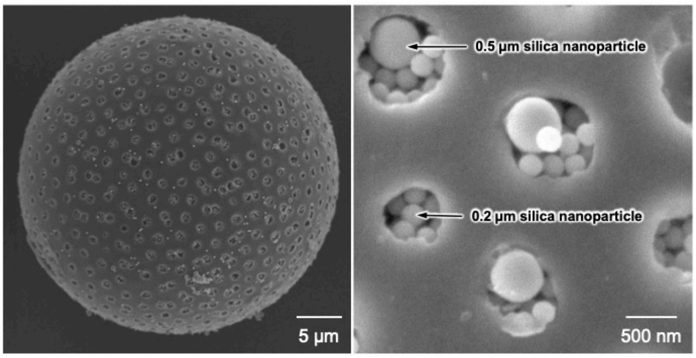


Figure 5. (a) SEM images of MS1.0-10@pSE with silica nanoparticles trapped inside the dimple structure.

Figure 6

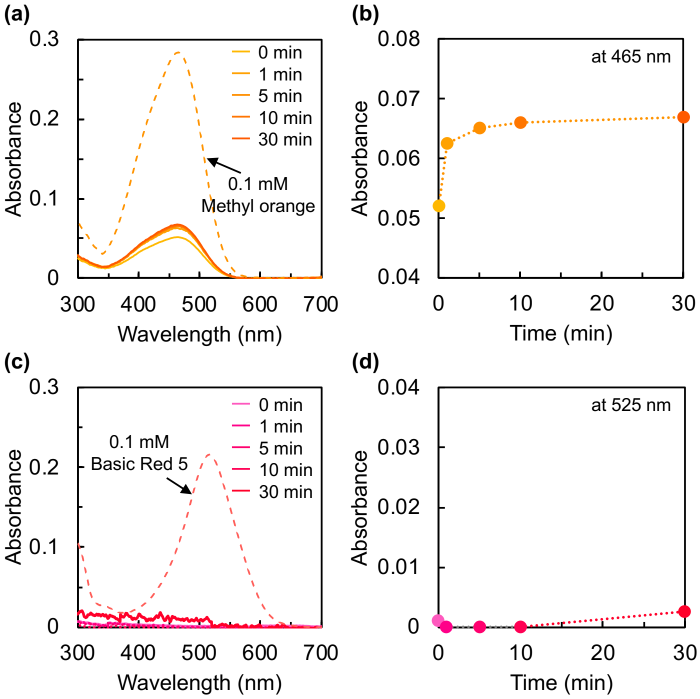


Figure 6. UV–Vis absorption spectra of dye solutions eluted from polymer particles (a,c) and secondary plots of the absorbance versus immersion time (b,d). a,b) Methyl Orange and c,d) Basic Red.

Figure 7

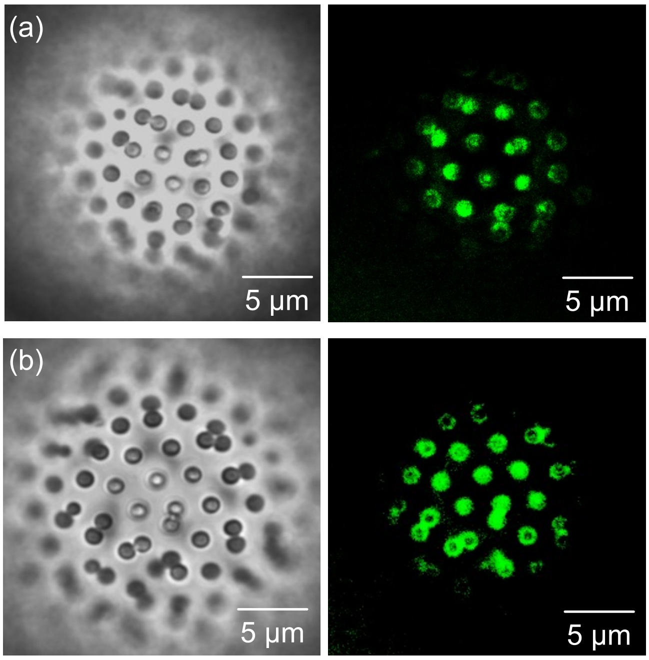


Figure 7. Confocal laser microscopy images of polymer particles with dye molecules adsorbed inside the dimple space: a) Methyl orange and b) Basic red.