

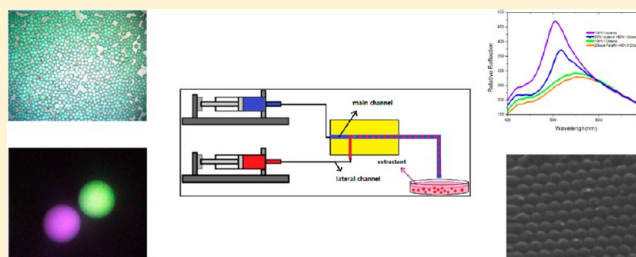
Extraction-Derived Self-Organization of Colloidal Photonic Crystal Particles within Confining Aqueous Droplets

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Supporting Information

ABSTRACT: In this work, we developed a novel and simple microfluidic method for the fabrication of self-assembled monodispersed photonic crystal microbeads with core-shell structures using solvent extraction. Monodispersed aqueous droplets encapsulating colloidal photonic crystal particles were produced in a T-junction microfluidic device, and the controlled transport of water from the aqueous droplets to the oil phase created spherical colloidal crystal microbeads with controlled shell-core structures by extraction-derived self-organization of the colloidal nanoparticles. While the solidification of colloidal particles from emulsion droplets in an oven took tens of hours, the present extraction-derived method reduces the time required for solidification to several minutes. Compared with recent microwave-assisted consolidation methods which showed a particle material dependency, our new method exhibited no such limitation. The results showed that the packing quality of colloidal crystals, which can be precisely controlled by adjusting the extraction rate and surfactant, was high enough to show photonic band-gap characteristics. The reflectance of our photonic microbeads responded precisely to any change in physical properties including the size of colloidal particles and refractive index. A mechanism of the extraction-derived self-assembly of colloidal particles was developed and then supposed by theoretical derivations and experimental results. Finally, the universality of the method was demonstrated by fabricating SiO₂ photonic crystal microbeads.



1. INTRODUCTION

Self-assembled materials have been attracting great attention for decades in a variety of fields including material science, chemistry, bioinstrumentation, and soft condensed-matter physics. In a self-assembled structure, the building blocks are organized spontaneously into bulk thermodynamic phases, often enabling the material to exhibit special optical properties. However, undesired defects are almost always unavoidable for most self-assembled structures. Furthermore, it is hard to control the quality of the ordered arrangement and packing structure. In the past, researchers have tried to introduce confined geometries to self-organization in order to prescribe lattice positions for the building blocks and control the bulk shapes and early research showed successful fabrication of relatively well-ordered structures of colloids with the confined geometry effect of microchannels¹ or capillary tubes.² Since then, an emulsion-based method for creating spherical-shaped monodispersed colloidal crystals and more complicated structures has been developed.³ In this method, the self-assembly process of colloidal particles is well-confined geometrically within monodispersed emulsion droplets. Confined colloidal particles in droplets could be self-organized into a spherical colloidal crystal⁴ (or photonic ball), exhibiting an optical stop band for any normal incident light homogeneously over the spherical surface because of the isotropic shrinking of droplets with slow evaporation of the liquid phase of the droplets. Optical beads produced in this method have been

applied in many fields, including biomolecular screening⁵ and bioassays.⁶ Nevertheless, a drawback of this method is the considerable length of time (~tens of hours) required for the process, and several researchers have tried to address this issue by using microwave irradiation to selectively heat the aqueous phase and reduce process time to tens of minutes.⁷ However, microwave irradiation carries a high energy cost and is limited in its application as polymer beads melt easily, leading to an uncontrollable red shift of the band gap. Furthermore, the assembling quality reduces remarkably as the fabrication process time is shortened with microwave irradiation, thus confining the final product potential applications.⁷

In addition to the need for a highly efficient and universal fabrication method, high quality colloidal crystal beads also require a specific and controllable size, a small size distribution, and good reproducibility. Recently, microfluidic methods have been developed for the controllable fabrication of monodispersed droplets, and many researchers have obtained highly monodispersed functional microparticles by using microfluidic methods.⁸ The microparticles produced in these studies have all the exhibited advantageous properties including controlled sizes (from 10 to 2000 μm diameter), narrow size distributions (a variation of less than 5%), and high reproducibility. To date,

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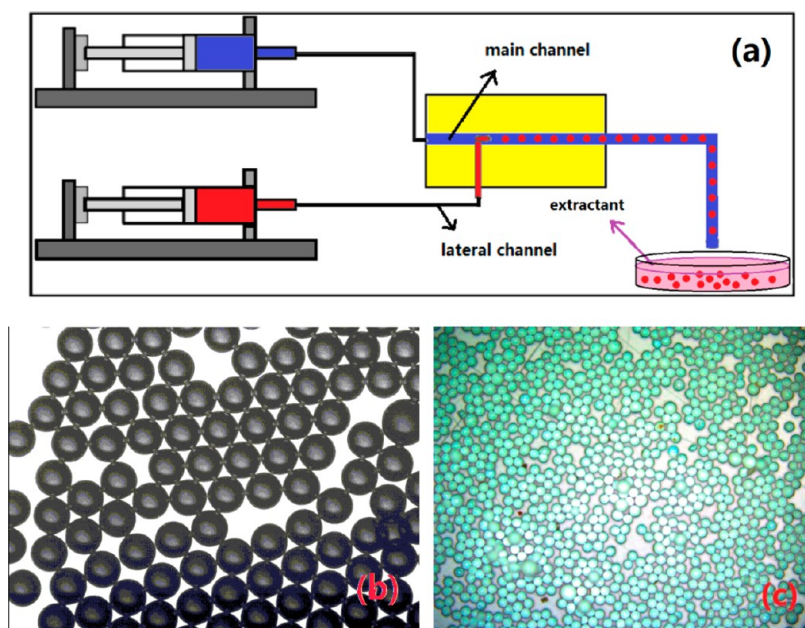


Figure 1. (a) The schematic diagram of the device for fabricating photonic microbeads in an extraction-derived method. (b) The monodispersed aqueous droplets produced from the T-junction, which contain colloidal PS particles of 200 nm in diameter. (c) Optical image of monodispersed photonic beads constructed by colloidal PS particles of 200 nm in diameter and extracted by 20 wt % *n*-butyl alcohol in 80 wt % *n*-octyl alcohol.

several studies have already demonstrated successful production of well-controlled photonic balls with complicated structures in microfluidic devices.⁹

In this article, we demonstrate that monodispersed colloidal particles inside emulsion droplets can be organized into core-shell colloidal crystal microbeads by combining microfluidic droplet formation and a solvent-extraction method. Solvent extraction has been used in the fabrication of functional materials¹⁰ for its remarkable efficiency and simplicity. In a water-in-oil emulsion, the oil phase acts as an extractant, and the water in the aqueous droplets diffuses into the oil phase, leaving the insoluble materials inside the shrinking droplet. If the residual materials can consolidate, a solid bead is obtained. Compared with conventional evaporation-derived consolidation, solvent extraction considerably reduces the time required for a complete consolidation of colloidal particles. Although the traditional thermodynamic equilibrium driven diffusion of water from the emulsion droplets to the continuous phase of silicone oil took tens of hours at room temperature for a complete consolidation, extraction-derived processes allow for the easy control of the transfer rate of water and can create spherical colloidal crystals in relatively short times (usually within 5 min). Furthermore, compared to the recently proposed method of microwave-assisted fabrication,¹¹ our new solvent-extraction method is more versatile and can be used for the fabrication of colloidal crystals of both silica and polymeric latex particles. Finally, this method is also conducive for controlling the packing density of latex particles, thereby tuning the photonic band gaps toward longer wavelengths.

In the subsequent sections, we describe the fabrication of uniform photonic crystal balls of polystyrene (PS) microspheres from uniform emulsion droplets generated in a T-junction microchannel. We also discuss how the extraction environment affects the shape and the packing quality of the colloidal particles in photonic balls made from water-in-oil emulsions, by examining the final products using reflectance spectrum, SEM images, and optical photos. A possible

mechanism is also proposed, considering the analysis of experiment results. Finally, we demonstrate that the method can also be used to successfully fabricate silica photonic beads.

2. PREPARATION OF MONODISPersed DROPLETS AND EXTRACTION-DERIVED CRYSTALLIZATION OF PS PARTICLES

2.1. Fabrication of Photonic Microbeads Using Microfluidic Devices. Uniform emulsion droplets on the micrometer scale can be produced using T-junction microfluidic devices,¹² and the size of the droplets is controllable.¹³ In this study, we used T-junction channels with a main channel diameter of 600 μm and a lateral channel diameter of 150 μm , as shown in Figure 1a. In these microchannels, the diameter of aqueous droplets produced could be easily controlled by changing the velocity of the two streams.

Monodispersed aqueous emulsion droplets were prepared by injecting an aqueous colloidal suspension of 1 wt % PS nanoparticles from the lateral channel into the main channel. The aqueous phase droplets are formed by the shearing of the dispersed phase by the continuous phase in the main channel. Upon exit from the microfluidic device, the droplets then flowed into the extractant in a Teflon dish. Detailed experimental procedures and materials are described in the Supporting Information. Monodispersed emulsion droplets ranging from 55 to 500 μm in average diameter were produced by simply changing the flow rates of the two phases. Figure 1b shows the optical micrographs of highly monodispersed emulsion droplets dispersed in hexadecane. The colloidal particles were consolidated into a spherical opaline structure as the water in the emulsion droplets was extracted. The consolidation time depends on the extraction environment, the concentration of the nanoparticles, and the size of the droplets. With 20 wt % *n*-butyl alcohol in 80 wt % *n*-octyl alcohol as the extractant, 1 wt % aqueous colloidal suspension of PS microspheres as the dispersed phase and the flow rate of main/lateral channel set as 10 $\mu\text{L min}^{-1}$ /500 $\mu\text{L min}^{-1}$, 45 μm diameter crystals with remarkable optical properties can be fabricated within 5 min, ~ 2 – 3 orders of magnitude faster than the traditional method of evaporation and about three times faster than the microwave-assisted method for fabrication of PS microbeads with similar optical properties. Optical micrographs of the microbeads are shown in Figure 1c. The microbeads were identified by a characteristic iridescent opaline color, clear evidence of the formation

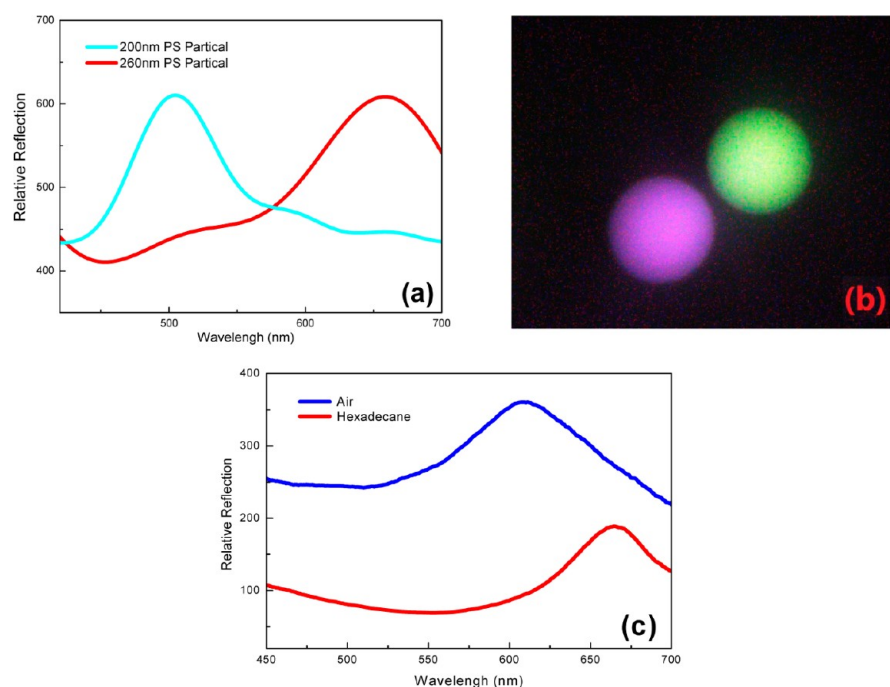


Figure 2. (a) The reflectance spectrum of microbeads construct of PS particles of 200 and 260 nm and infiltrated in hexadecane. (b) An optical image of the two kind of microbeads noted in Figure 2a, which are sized 45 μm in diameter. (c) The reflectance spectrum of microbeads constructed of PS particles of 260 nm infiltrated in air and hexadecane.

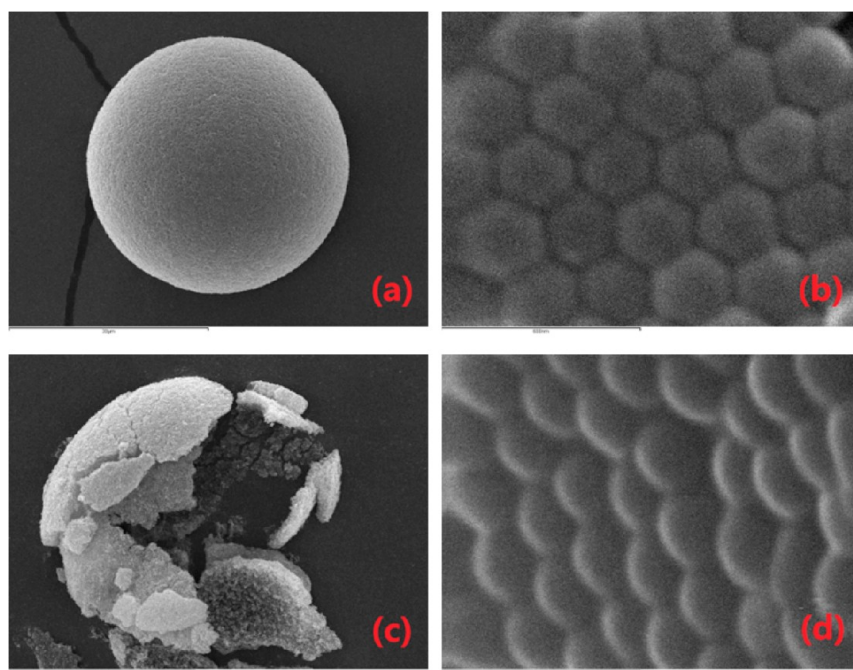


Figure 3. SEM images of microbeads constructed by colloidal PS particles of 200 nm in diameter and extracted by 20 wt % *n*-butyl alcohol in 80 wt % *n*-octyl alcohol. (a) An intact bead. (b) Partial surface of (a). (c) A broken microbead with a core–shell construction. (d) Partial inner surface of (c).

of spherical colloidal crystals or photonic balls. SEM was also used to effectively characterize the microbeads.

2.2. Characterization and Test of the Fabricated Crystal Balls. The Bragg's Law for microbeads was used to verify whether the microbeads produced using the new method were photonic crystals:⁷

$$\lambda = 2dn_{\text{eff}} = \left(\frac{8}{3}\right)^{1/2} D \left(\sum_i n_i^2 V_i\right)^{1/2} \quad (1)$$

where λ is the wavelength of reflected light, n_i the refractive indices of the two phases, V_i the volume fraction, d the characteristic spacing, and D , the particle size. In accordance with Bragg's law, we can calculate the reflective wavelength, λ , with different D or n_i if the surface of the spherical ball is assumed to be in the (111) plane of the fcc packing symmetry. To measure the reflectance spectrum, different-sized PS photonic particles of 200 nm and 260 nm with a refractive index of $n = 1.59$ were dispersed in different media including air and hexadecane, refractive indices $n = 1.0$ and 1.43, respectively. As shown in Figure 2,

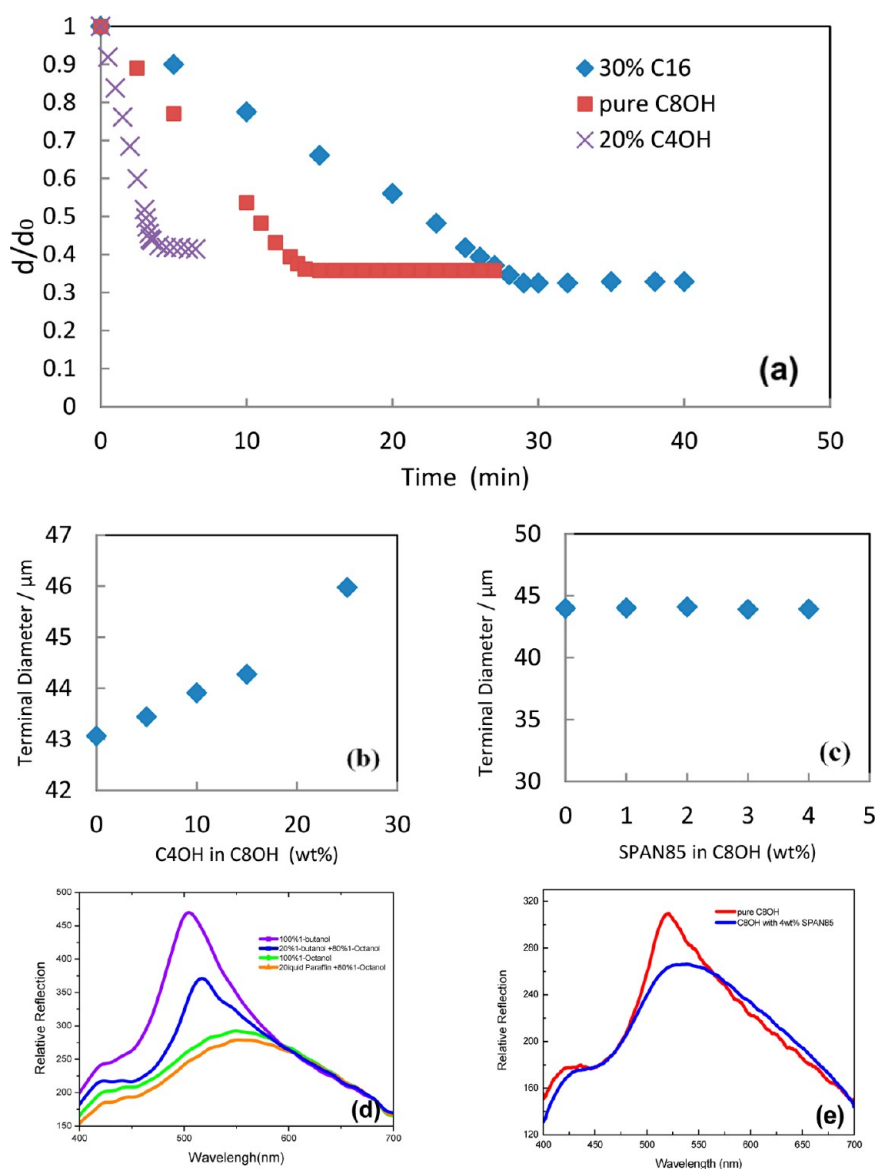


Figure 4. (a) Size change of the emulsion droplets with the three extractants noted in the diagram. Monodispersed PS particles of 200 nm in diameter were dispersed inside of the aqueous emulsion droplets. (b) The terminal diameter of emulsion droplets which contained 200 nm PS particles after extraction with different concentrations of *n*-butyl alcohol in *n*-octyl alcohol. (c) The terminal diameter of emulsion droplets which contained 200 nm PS particles after extraction with different concentrations of SPAN 85. (d) Reflectance spectrum of microbeads extracted by 20 wt % *n*-butyl alcohol in *n*-octyl alcohol, by pure *n*-octyl alcohol and by 30 wt % hexadecane in *n*-octyl alcohol. (e) Reflectance spectrum of microbeads extracted with and without 4% SPAN85 noted in (c). All the reflectance spectrum were measured when the microbeads were infiltrated in hexadecane.

the reflectance peak follows Bragg's law precisely. By immersing the microbeads fabricated with nanoparticles 200 nm and 260 nm in diameter into hexadecane, we obtain different reflectance peaks at 510 ± 3 nm and 659 ± 3 nm, while the calculated values were 507 nm and 658 nm, respectively. When dried microbeads fabricated with 260 nm particles were placed into air and hexadecane, two peaks of 620 ± 3 nm and 659 ± 3 nm were observed, while the calculated values were 619 nm and 658 nm. The consistency between calculated values and the experimental measurements shows that the products are qualified in optical properties. In addition, the microbeads exhibited uniform sphericity with a narrow size distribution.

Figure 3 (panels a and b) show the SEM images of photonic crystal microbeads with a diameter of 45 μm fabricated using 260 nm PS nanoparticles. Upon a more detailed examination of the surfaces of the microbeads, an array of highly ordered packing was observed explaining the microbeads' optical properties. Remarkably, we also observed a universal core-shell structure shown in Figure 3 (panels c

and d). Such a core-shell structure has a high usage of the monodispersed nanoparticles. By arranging them in such core-shell structure, one could use fewer nanoparticles to fabricate a photonic bead with a requested size. Furthermore, as photonic crystals made with certain materials could be used as a photocatalyst, a core-shell structure might greatly enhance the efficiency of the catalyst.¹⁴

3. EFFECT OF THE EXTRACTANT ON THE STRUCTURES OF PS CRYSTAL MICROBEADS

In this section, we discuss how the extractant process affects the properties of the microbeads. In Figure 4a, the diameter of emulsion droplets which contained 200 nm PS nanoparticles is plotted against the extraction time for different extractants (indicating different extraction rates). As noted, two distinct stages were observed: at first, the size of the emulsion droplets was reduced nearly linearly for a relatively long period of time,

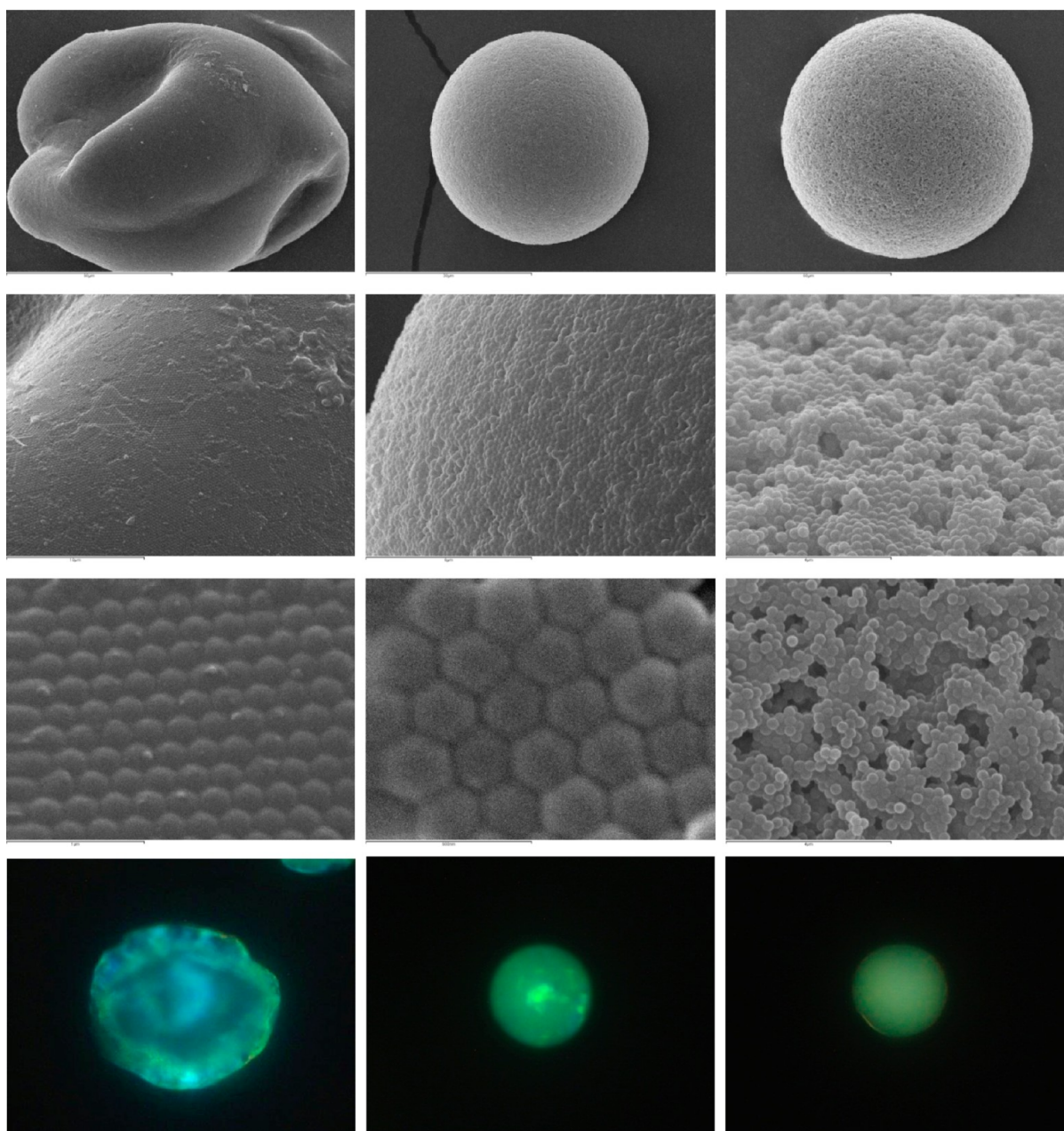


Figure 5. SEM images and optical photos of the spherical colloidal crystals composed of monodispersed PS particles of 200 nm in diameter at various magnifications. The three lines show three kind of beads that extracted in different extractants noted on the top. The first row shows an overall perspective; the second shows the partial surface, and the third shows a close-up of the details of the beads' surface to see the arrangement of the particles. The last row shows the optical photos under reflectance light, corresponding to the above SEM images.

closely resembling the behavior of pure water droplets. However, after a certain period of time, the droplets stop shrinking, indicating consolidation of its surface. As the extraction rate was enhanced by changing the extractant components, we observed not only faster consolidation but also an increase in the final diameter. By changing the *n*-butyl alcohol concentration in *n*-octyl alcohol from 0 to 25 wt %, the final diameter of the microbeads increased by 10% (from 44 to 48 μm), as shown in Figure 4b. However, no similar phenomenon was observed upon changing the concentration of surfactant SPAN 85 from 0 to 4 wt %, as shown in Figure 4c.

We also investigated the reflectance spectrum of same-sized microbeads fabricated using different extractants to determine any differences in optical properties. In Figure 4d, 45 μm

microbeads made of 200 nm PS particles are extracted by 20 wt % *n*-butyl alcohol in 80 wt % *n*-octyl alcohol with and without the 4 wt % SPAN-85 surfactant, immersed in hexadecane during characterization. Although the concentration of SPAN-85 only slightly affects the macroshape of the beads, it markedly influences their reflectance properties. The microbeads extracted without surfactants maintain a stronger and sharper reflectance peak than those produced with 4% SPAN, indicating that the surfactant may have a negative effect on the highly ordered packing necessary for PS particle photonic crystals. This may be caused by the steric hindrance and the more viscous interface brought about by the high-molecular weight surfactant.

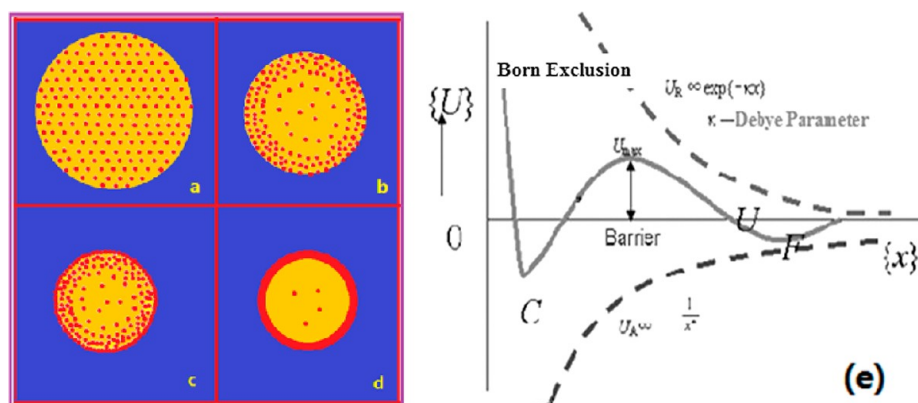


Figure 6. (a–d) The schematic diagram to illustrate the extraction process from the beginning of extraction to terminal consolidation. (e) The curve of potential energy between colloidal particles, where the upper phase means exclusion.

We also tested the optical performance of microbeads fabricated at different extraction rates. Pure *n*-butyl alcohol, 20 wt % *n*-butyl alcohol in 80 wt % *n*-octyl alcohol, pure *n*-octyl alcohol, and 20% hexadecane in 80 wt % *n*-octyl alcohol were used as the extractants, with the size of initial droplets being the same at 252 μm . All products were immersed in hexadecane during the characterization. As shown in Figure 4e, the quality of the optical property is positively correlated with the extraction rate; the microbeads produced using the first two extractants maintain prominent reflectance peaks, while the reflectance peaks of the microbeads extracted using the last two extractants are so wide that they can hardly be used in any optical device. Additionally, we observed a red shift of the reflectance peak when we reduce the extraction rate. For the four different extractants mentioned above, the peak positions were measured at 505 ± 3 , 510 ± 3 , 536 ± 3 , and 548 ± 3 nm, respectively, while the wavelength calculated using Bragg's law was 507 nm. The first two extractants follow Bragg's law precisely. From the SEM images and optical photos shown in Figure 5, we can compare the macro- and microstructures of microbeads extracted using different extractants. Although the sphericity of the microbeads extracted with *n*-butyl alcohol was poor due to the collapse of the shell which was too thin to support itself under a relatively fast shrinking rate,¹⁵ the microbead surface is nevertheless highly ordered with little difference from an elaborate photonic crystal film fabricated over the course of days.¹⁶ Conversely, the microbeads made with 20% hexadecane in 80 wt % *n*-octyl alcohol exhibited excellent sphericity but with a rather disordered surface as shown by SEM. The microbeads extracted with 20 wt % *n*-butyl alcohol in 80 wt % *n*-octyl alcohol, however, exhibited a good spherical shape as well as a highly ordered surface packing. The extraction conditions are therefore very important for determining the microbeads optical characteristics and their potential for use as color pigments, scatterers, and diffusers.

4. MECHANISM OF EXTRACTION-DERIVED CRYSTALLIZATION

From the experimental results, we found that both the size of and the optical properties of the produced crystal microbeads are positively correlated with the strength of the extraction, contrary to the findings in a previous study^{11b} where the authors employed microwave-assisted evaporation of colloidal droplets to minimize process time at the expense of yielding poorer optical properties. Intuitively, the self-assembly process,

in which thermodynamic factors dominate, should favor a slower and longer formation process to promote assembly quality allowing colloidal particles more time to organize into a static position. However, according to the experimental results, this is not the case and a clear explanation of the underlying mechanism driving extraction-derived crystallization processes is required.

4.1. A Proposed Explanation for the Core–Shell Structures. In order to better understand the mechanism, we first analyzed the core–shell structure which is not typically observed in traditional long-term evaporation-derived self-assembly processes. In a previous study,¹⁷ researchers fabricated colloidal crystal microbeads using fluorescent microspheres measuring 1.2 μm in diameter, in order to observe the inner structure of beads assembled in minutes with microwave-assisted heating. They found that the microbeads exhibited a closely packed outer structure and a loosely packed inner array, corresponding to the core–shell structure observed using our extraction-derived method. The essential difference between the traditional long-term method and our method is the rate at which droplets shrink due to evaporation. Our extraction-derived method is more than 100 times faster than the evaporation-derived method, and the core–shell structure is likely formed due to the rapid shrinking of the interface.

Consequently, the relationship between extractant and the final structure of the microbeads can also be explained by the influence of the droplet shrinking rate. One possible mechanism for the core–shell structure formation can be determined by observing the coefficient of the interface-shrinking-derived concentration and the potential energy characteristics of these colloidal nanoparticles. Transitioning from a state of steady dispersion to a state of coagulation, colloidal particles with a relative high energy input must approach each other closely enough to overcome an energy barrier (noted in Figure 6e) before they can spontaneously coagulate. The energy input is needed to reach a critical concentration. In addition, the considerably rapid shrinking of the droplet creates a nonuniform distribution of PS nanoparticles, such that the concentration is always higher near the interface than near the center because the particles near the interface do not have enough time to diffuse to the inner part of the droplet. Thus, the region near the interface can reach the critical concentration sooner than the center of the droplet, causing consolidation in the form of a shell. As the extraction rate slows, nanoparticles gradually attach to the shell, leaving an empty core inside. Accordingly, the faster the extraction is, the greater the

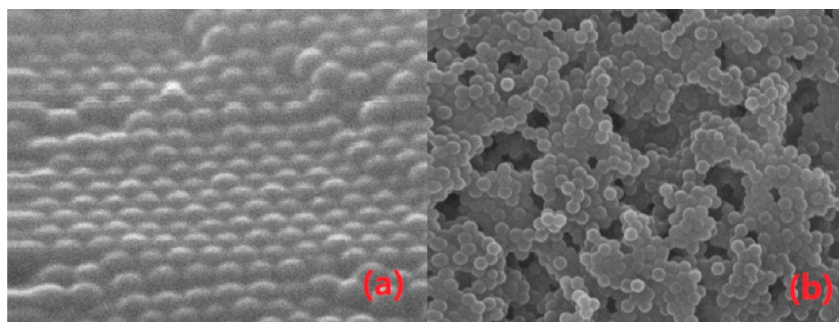


Figure 7. SEM images of 45 μm microbeads extracted in different extractants: (a) 70% butyl alcohol in octyl alcohol and (b) 30% hexadecane in octyl alcohol.

concentration difference inside the droplets would be, and the larger the final diameter of the beads would be. The whole extraction process is expressed in Figure 6 (panels a–d).

4.2. Comparison of the Interface-Motion and the Particle Diffusion. To illustrate that the moving of the interface can significantly affect the self-assembly of the colloidal nanoparticles, we take the diffusion coefficient of colloidal particles^{8c} into consideration,

$$D = \frac{kT}{6\pi\eta} \quad (2)$$

where the temperature is 298 K, with water as the solvent ($\eta = 1.0 \times 10^{-3} \text{ Pa s}$). Assuming that the diameter of the solvated particle is approximately the same as the microbead particles' diameter (200 nm), we can then calculate that $D = 1.0 \times 10^{-13} \text{ m}^2/\text{s}$. According to the Fick Law describing the diffusion process, we have

$$J = -D \frac{d\rho_v}{dx} \quad (3)$$

where J is the mass transfer flux density measured in volume and ρ_v is the volume density of colloidal particles. The mass transfer flux density can be calculated as $J = u * \phi$, where u is the moving speed of the interface and ϕ is the volume fraction of the nanoparticles. So, we can obtain the characteristic size of a droplet with which size the moving interface matches the diffusion of nanoparticles,

$$l = \left| \frac{\rho_v}{\frac{d\rho_v}{dx}} \right| = \frac{D * \rho_v}{u * \phi} \quad (4)$$

At the point of consolidation in a well-ordered structure, the volume fraction of colloidal nanoparticles, $\phi = 0.7418$, and in the whole process, we have $\rho_v < \rho_v(\text{max}) = 0.74 \text{ m}^3/\text{m}^3$. The moving speed of the interface in the extraction process between octyl alcohol and water is $u = 8.3 \times 10^{-8} \text{ m/s}$. Thus, the maximum size of the droplets in which the moving speed of interface is not much faster than the diffusion of colloidal nanoparticles is approximately,

$$l(\text{max}) = \frac{D * \rho_v(\text{max})}{u * \phi} = 1.2 \mu\text{m} \quad (5)$$

However, the droplets in our experiments were at least 40 μm , much larger than the calculated $l(\text{max})$, showing that the interface moves much faster than the diffusion of the nanoparticles in the droplets. As a result, the colloidal nanoparticles are distributed much more densely near the

interface than in the inner part of a droplet because the nanoparticles cannot diffuse faster than the velocity of the quick-moving interface. The boundary near the interface reached the critical consolidation concentration first, forming a shell. The faster the interface moves, the more nonuniform the nanoparticles are distributed and the larger the diameter of the final microbeads obtained. Thus, microbeads with a thinner shell and a bigger core could be fabricated. In conclusion, the size and the core–shell structure of the photonic beads can be controlled by adjusting the extraction intensity and speed with which the droplet interface shrinks.

4.3. Mechanism of Nanoparticles' Self-Assembly with Relatively High-Rate Interface Motion. The more uniform the array of nanoparticles is, the better optical properties the microbeads would have. In the traditional long-term fabrication process, the shrinking is so slow that the quality of assembly is determined by their ability to maintain the unclosed packed three-dimensional (3D)-ordered array of nanoparticles. Relative study has verified this effect,^{18,19} which is a consequence of the particles' similar electronic repellent against each other. However, in our new process, the shrinking is so fast that it results in “forced interfacial adsorption”, a phenomenon with greatly uneven distribution of nanoparticles toward the interface, which is sure to affect the mechanism driving the self-assembly process. The “adsorbed” nanoparticles would still present some kind of ordered array near the interface (instead of around the droplet as a whole) because of their electronic repellent, but such stability is positively related to the “absorption force”, namely the shrinking rate of the interface. The faster the interface shrinks relative to the diffusion of nanoparticles, the rarer the interchange and disturbance frequency of the array near the interface would be in the process, the more steady the forced absorption would maintain, and lastly, the better the final assembly that would be obtained.

SEM images could confirm the proposed mechanism. In the case of using an extremely fast extractant, 70% butyl alcohol in octyl alcohol for example, the limited time allowed for diffusion of nanoparticles between the outer and inner parts of the droplet limits the lattice interchange frequency, stabilizing the colloid nanoparticle array near the interface and leading to a preferable interface self-assembly, as shown in Figure 7a. In the case of using an extractant which is not strong enough, 30% hexadecane in octyl alcohol for example, the relatively considerable ability of the nanoparticles to diffuse would disturb the array near the interface, and finally would lead to defects and vacancies in the final lattice structure of the microbeads, resulting in degradation of the optical properties or

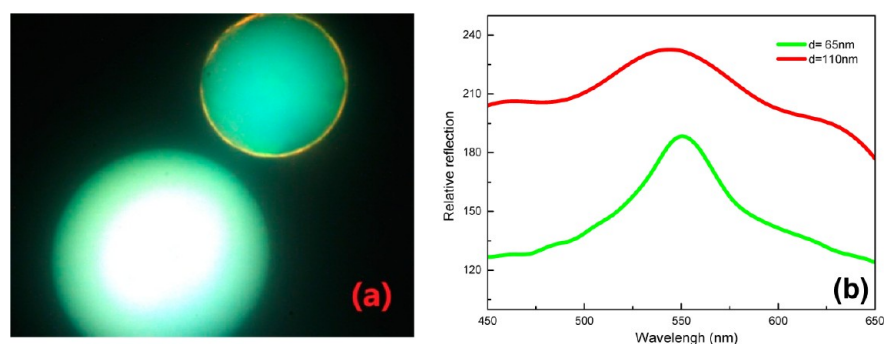


Figure 8. (a) Optical images and (b) reflectance spectrum of microbeads with sizes of 65 and 110 μm .

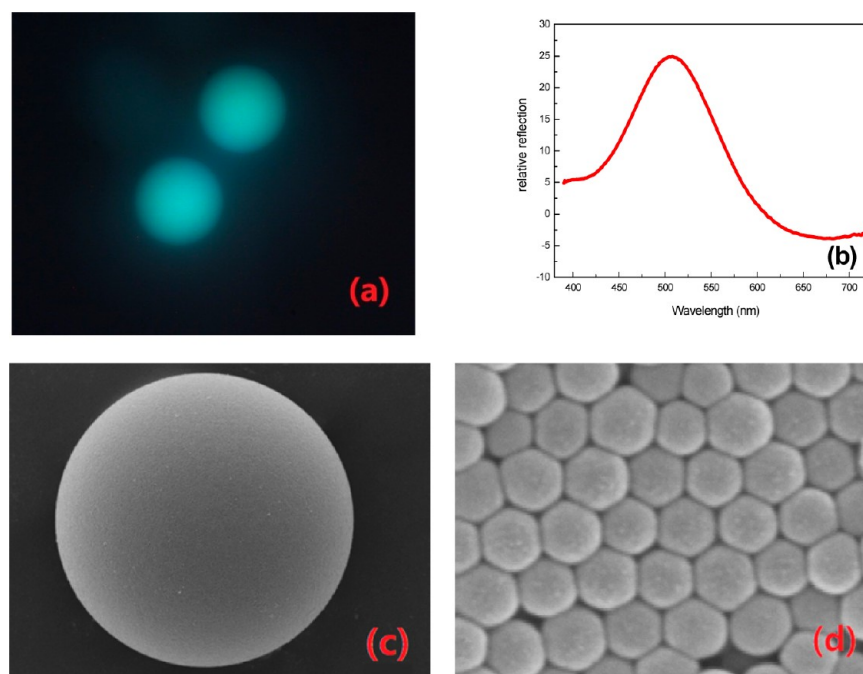


Figure 9. (a) The optical image of the microbeads made by silica nanoparticles. (b) The reflectance spectrum of the microbeads. (c) The SEM image of a silica bead, where the scale bar is 50 μm . (d) The SEM image of the surface detail of a microbead showing the highly ordered structure, where the scale bar is 700 nm.

even a red shift in the reflectance spectra, as shown in Figure 7b.

The mechanism for colloidal consolidation resulting in a core–shell structure should be independent of the method used to extract water and should therefore apply to all cases in which the motion of the shrinking interface is much faster than the diffusion of the nanoparticles. It should be noted, however, that there are several factors that potentially increase the diffusion rate of the nanoparticles within the droplet. If these factors significantly enhance nanoparticle diffusion, the positive correlation mentioned above between extraction rate and self-assembly quality may not hold. For example, if high-intensity microwaves were used to heat the system, it is possible that gasification may occur at some points inside the droplets. Such gasification points can generate disturbances inside the droplets which increase the diffusion rate of the particles and accelerate the mixing between the outer and inner regions.

4.4. Verification of the Proposed Mechanism. In order to further examine our hypothesis, we derived some generalizations from our proposed mechanism and then examined these generalizations with corresponding experiments. First,

according to the mechanism, the size of the initial droplet should affect the microbeads' final optical properties. With the original concentration fixed, in a droplet with a constant shrinking rate (measured by diameter) as shown in Figure 4a, the smaller the droplet size, the more intense the density concentration process would be because density concentration decreases cubically with diameter. A faster density concentration process would enhance the stability of forced adsorption near the interface and reasonably improve the assembly quality and optical properties. In the corresponding experiments, we fabricated microbeads of different sizes (65 and 110 μm) from suspensions with the same concentration in the same extractant bath. From the optical image and the reflectance spectrum shown in Figure 8, the smaller microbeads show more exact chroma and sharper spectrum peaks. Second, we assume that the surfactant in the extractant, SPAN 85, could be absorbed on the oil–water interface and even could diffuse into the inner phase, making nanoparticles attached to the interface more difficult to rearrange. Furthermore, a high-concentration of surfactant resulting in micelles of considerable size (about tens of nanometers or more) around the interface might play a role

in steric hindrance, disturbing the self-assembly of the PS colloidal nanoparticles. This explanation coincides with our experiments very well, shown in Figure 4e.

In conclusion, we developed a mechanism analysis both for the formation of core–shell structure and the self-assembly of nanoparticles in our solvent-extraction-derived consolidation process for the fabrication of optical microbeads. The nonuniform distribution of colloidal nanoparticles in the droplets caused by the rapid motion of the interface is a unique property and advantage of the extraction method. By adjusting the extraction rate or the original size of the droplets, the thickness of the shell, the nanoparticle packing quality, and the optical quality of the microbeads could be controlled. With an increase in the stability of the forced-interface-adsorption, a better assembly process could be obtained.

5. PREPARATION OF SiO_2 COLLOIDAL MICROBEADS

We also used the microfluidic method described above to prepare SiO_2 colloidal microbeads. The SiO_2 suspension was 1 wt % SiO_2 monodispersed nanoparticles (220 nm in diameter, CV = 6%) in water with 50 ppm NaN_3 as a stabilizer after 4 h of ultrasonic mixing. The refractive index of the nanoparticles was 1.46. *N*-octyl alcohol was used as the extractant and a batch of blue microbeads was then fabricated. As shown in Figure 9a, when the microbeads were immersed into hexadecane, a reflectance peak was observed at 510 nm, precisely fitting Bragg's law, indicating the successful fabrication of photonic microbeads.

These experimental results demonstrate that our extraction-derived method is applicable not only for the fabrication of PS photonic balls, but also for silica photonic balls, without considerable degradation of the photonic properties.

6. CONCLUSIONS

In this article, we developed a novel and versatile method for the preparation of self-assembled monodispersed photonic crystal microbeads with core–shell structures by combining microfluidic droplet formation with an extraction-driven solidification method. Monodispersed aqueous droplets encapsulating colloidal photonic crystal nanoparticles were produced in a T-junction microfluidic device, and the controlled transport of water from the aqueous droplets to the oil phase produced spherical colloidal crystal microbeads with controlled shell–core structures by quickly concentrating self-organizing colloidal nanoparticles in the outer regions of the drop, using a fast extraction process. With the use of an appropriate extractant, the emulsion droplets were consolidated into high-quality photonic crystal microbeads in a very short time period compared to other reported methods. The photonic crystal microbeads fabricated in strong extractants without surfactant showed a well-ordered packing and good optical properties. The reflective colors depended on the size of the constituting nanoparticles and the refractive index contrast. However, the photonic balls displayed an identical reflective color for normal incident light because the surface of the photonic balls was in the (111) plane of fcc packing. We could control the packing density of photonic balls by changing the extraction rate to tune the photonic band gaps and reflective colors. A possible mechanism was proposed to explain the experimental results. The photonic balls produced can be used as highly functional pigments, biosensors, and light diffusers. Moreover, if the number of the constituent nanoparticles in

each droplet is small, we can also fabricate colloidal clusters which are useful as colloidal photonic molecules.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details are described including materials, experimental procedures, and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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