

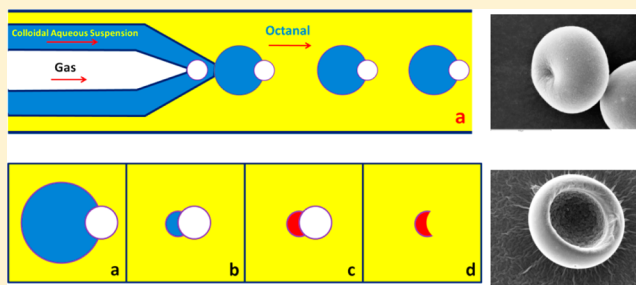
A Novel Method of Fabricating, Adjusting, and Optimizing Polystyrene Colloidal Crystal Nonspherical Microparticles from Gas–Water Janus Droplets in a Double Coaxial Microfluidic Device

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S Supporting Information

ABSTRACT: The optical properties of close-packed polystyrene colloidal crystal particles could be improved and controlled via adjusting their shape, by first forming colloidal suspension–gas Janus droplets with different structures in a double coaxial microfluidic device, and then solvent-extraction-derived self-assembly to form nonspherical microparticles with different shapes.



Self-assembled colloidal crystals are attracting great attention in various fields, including chemistry, material science, bioinstrumentation, and sensor technology. Colloidal crystals are organized spontaneously by monodispersed colloidal particles into bulk thermodynamic phases, exhibiting special optical properties.¹ Nonclose-packed and close-packed colloidal crystals have both been recently studied.¹ The close-packed colloidal crystals have advantages such as relatively sharper and more stable optical peaks and more simplified fabrication, compared with the nonclose-packed ones. In fact, many researchers have applied close-packed colloidal crystals into biomolecular screening and bioassays.² For further application of colloidal crystals, we always need to shape it into particles with ease and confined geometries have been introduced into self-organization in order to control the bulk shapes. Early research showed successful fabrication of relatively well-ordered structures of colloidal particles with the confined geometry effect of microchannels or capillary tubes, where confined colloidal particles in droplets could be self-organized into spherical colloidal crystal particles (or photonic beads) after removing the solvent.³

There are three key problems in fabricating monodispersed close-packed colloidal crystal particles (CCCP) from droplets of colloidal suspension. The first problem is to ensure the monodispersity of the particles, the second is to improve the efficiency of the fabrication process, and the third is to establish a way to control and optimize the CCCP's optical properties.

The first problem, monodispersity, is solved successfully by introducing microfluidics devices. Microfluidics has been used to form uniform complex emulsion, and further to fabricate monodispersed functional materials,⁴ because of its excellent potential to easily control the size and the structure of the droplets by adjusting the design of the microchannels and the flux of each phase.⁵ Researchers have produced monodispersed

spherical CCCP with microfluidics devices.^{2,6} However, they usually used evaporation-derived methods to remove water in aqueous colloidal suspension droplets and then to make the colloidal particles inside the droplets self-assemble. Although the CCCP's optical properties are good by using this fabrication method, its disadvantage is also considerable: it always costs tens of hours just to fabricate a batch of CCCP, the size of which is just tens of micrometers.

Recently, there are two approaches in accelerating the self-assembly process inside aqueous droplets. Kim et al.^{6b} introduced microwave irradiation into the system to selectively heat the water molecules, which accelerates the evaporation process to tens of minutes. However, microwave requires a high energy cost and has a material-limitation, as polymer beads melt easily under this irradiation. In order to overcome these shortcomings, Xu et al.⁷ proposed a relatively efficient, simplified, and universal method to fabricate spherical CCCP. In our previous work, we got monodispersed aqueous suspension of colloidal in a T-junction microchannel and then utilized a solvent-extraction method to remove the water in droplets to derive the self-assembly of the colloidal particles quickly. By using lower alcohol as an extractant, we could obtain products with both uniform shape and good optical properties in less than 10 min and it could be applied to more systems. We also discussed the self-organization mechanism in rapidly shrinking droplets, and find that, in such strongly dynamic process, the packing quality is positively related to the relative extraction strength (or, in micro perspective, the stability of forced absorption of colloidal particles on the shrinking interface), which is the cofunction of extractant, the

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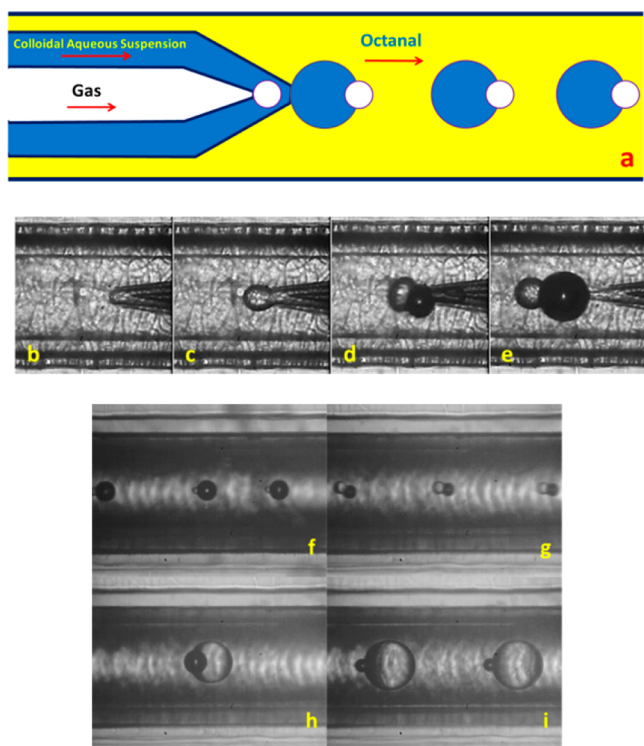


Figure 1. Schematic diagram of the process to fabricate nonspherical colloidal crystal particles. (a) Janus droplets are formed in a double coaxial microfluidic device. (b–d) Optical images of the droplet formation process. (f–i) Different Janus droplets, where the aqueous droplets are surfactant-saturated water without colloidal particles. (f) Relatively large bubbles and small aqueous droplets, where the flow rates of continuous phase, aqueous phase, and gas phase are 600, 0.1, and 5 $\mu\text{L}/\text{min}$, respectively. (g) Bubbles and aqueous droplets with similar size, where the flow rates are 600, 1, 1 $\mu\text{L}/\text{min}$, respectively. (h) Relatively larger droplets and smaller bubbles, where the flow rates are 600, 10, 1 $\mu\text{L}/\text{min}$, respectively. (i) Small bubbles with extremely large droplets, where the flow rates are 600, 30, and 0.1 $\mu\text{L}/\text{min}$, respectively.

specific surface of the droplets and the concentration of the colloidal particles. If we could create and control such a strong extraction environment, even if partially on the droplets, we may then optimize and control the optical properties of the photonic beads easily. However, there is still a key problem with this method. Although we could get very-high-packing quality with a very strong extraction, the shape of the whole particle becomes hard to control in that case.

Herein, we introduce a novel method to solve the problem, following the principles found in our previous work, by introducing a third phase, gas bubbles, to attach on the aqueous colloidal suspension droplets when forming the droplets in a double coaxial microfluidic device. The attachment of a microbubble on a droplets, which is also called the formation of a “Janus droplet”, will create a triphase interface on different sides of which the mass transfer rate across the interface are not the same, leading to a “coffee ring” effect⁸ in such aqueous droplets that contact both gas and extractant. This creates circumflux inside the aqueous droplets which might lead to a concentrating of colloidal particles toward the triphase interface. Consequently, we might optimize the integral optical properties of CCCP by forming Gas–Water Janus droplets in the extractant. If we could further adjust the structure of the Janus droplets in order to control the relative area of the

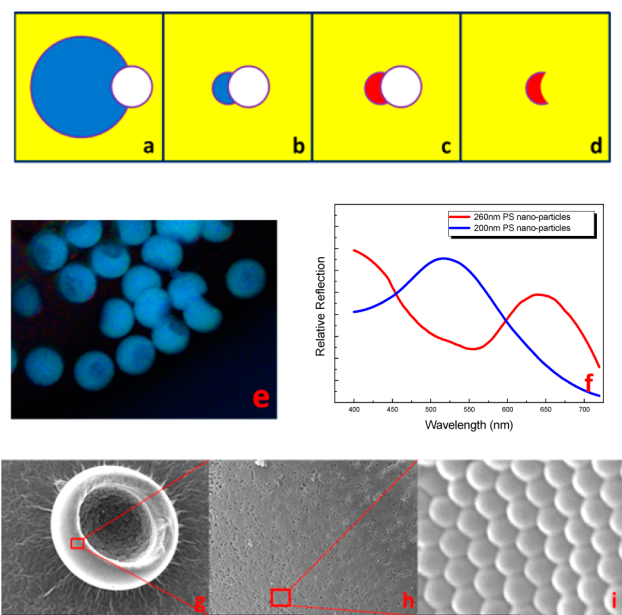


Figure 2. The extraction process and the products. (a–d) The schematic image of the extraction process: (a) Janus droplets are positioned into the extractant. (b) Water is removed by the extractant and the aqueous part of the Janus droplet shrinks, while the bubble keeps its volume. (c) The colloidal particles start to crystallize into a solid. (d) The bubble is removed, and the nonspherical particle is finally produced. (e) The optical image of nonspherical colloidal crystal particles, packed with 200 nm PSt colloidal particles. (f) The reflection spectra of nonspherical particles packed with 200 nm (blue) and 260 nm (red) PSt colloidal particles. (g) SEM image of a typical bowl-like photonic microparticle, where the scale bar is 100 μm . (h–i) Details on the surface of the particle shown in (g), where the scale bars are 7 μm and 600 nm.

triphase interface, we might then control the integral optical properties of CCCPs.⁸

In the experiments, we chose octanol as the continuous phase, water mixed with 0.5 wt% Tween 80 and 0.1 wt % to 1 wt % PSt colloidal particles as the dispersed aqueous phase extractant, and air as the gas phase. We could find that this system could satisfy the relationship to form the Janus droplet (see Table S1 of the Supporting Information).

The key of the first step is to controllably form the Janus droplets. Recently, many researchers have started to work on formation of complex emulsions with Janus structure and further on fabrication of Janus multifunctional materials,⁹ and even multifunctional CCCP.^{6a,c,d} In this work, we realize the formation of Janus droplets in a so-called double coaxial capillaries device, a schematic diagram is shown in Figure 1a. Some researchers have utilized similar devices to fabricate G/W/O double emulsions.¹⁰ Herein, octanol, the continuous phase, flows in the outer channel which is a glass capillary. The middle channel contains the aqueous suspension of PSt colloidal particles, whose diameter is 200 or 260 nm and whose concentration changes from 1 to 0.1 wt %. Air is pumped into the inner channel through a glass capillary, whose diameter at the tip is about 10 μm . The aqueous droplet and the gas bubble break from the tip together and attach on each other to form the Janus structure, and a classic process is shown in Figure 1, panels b–e). In our experiments, the relative standard deviation of the droplet size is less than 5%.

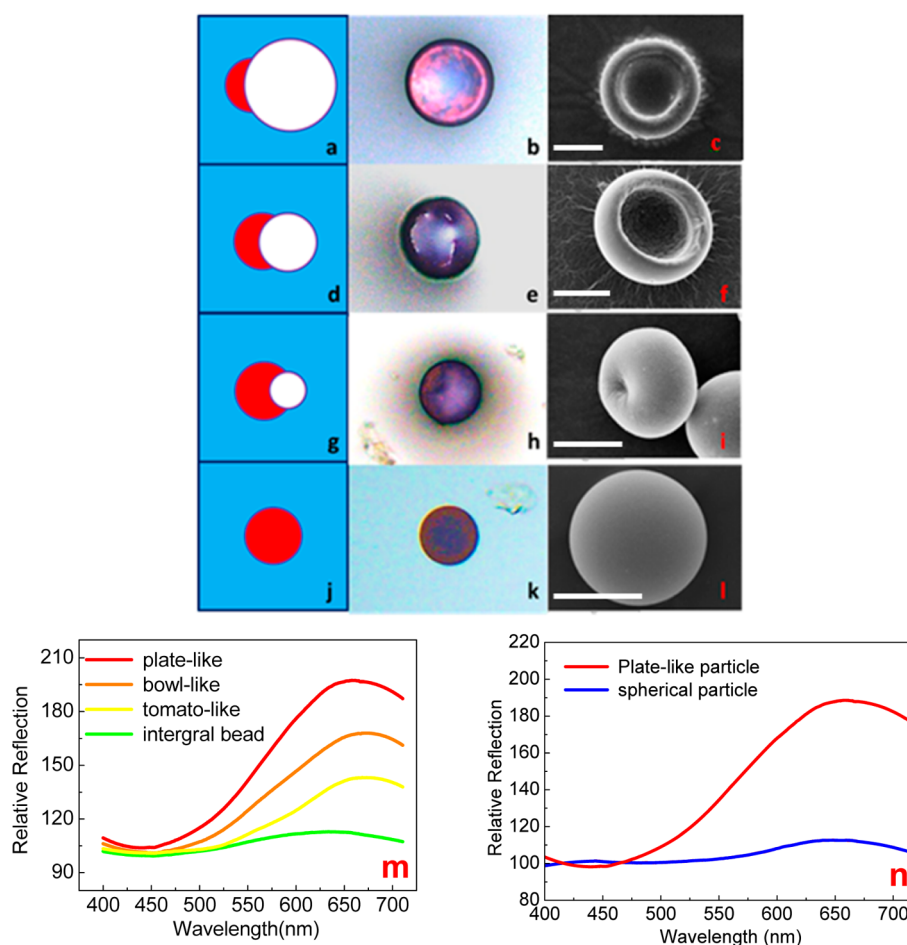


Figure 3. (a–i) Schematic diagrams, optical images, and SEM images of colloidal crystal particles of different shape, where the scale bars of SEM image is $120\ \mu\text{m}$: (a–c) platelike, (d–f) bowl-like, and (g–i) tomato-like, where the scale bar is $100\ \mu\text{m}$. (j–l) Spherical. (m) Comparison of reflection spectra for particles of different shapes. (n) Comparison of reflection spectra between the platelike particles extracted by octanol and the spherical particle extracted by 20% *n*-butyl alcohol in 80% octanol. All particles presented above are packed with 260 nm PSt colloidal particles.

The structure of droplets could be controlled by adjusting the three-phase flow rate independently (see Figure S1 of the Supporting Information). In this work, we successfully and controllably formed Janus droplets of different shapes, from big-bubble–tiny-droplet to tiny-bubble–big-droplet, as shown in Figure 1, panels f–i). After solvent extraction, these different shapes of Janus droplets would become photonic microparticles with different shapes.

After forming the monodispersed Janus droplets, these droplets are positioned in an extraction dish full of extractant. Water in the aqueous droplets is gradually removed outward to the extractant. When the extraction is finished, colloidal particles start to crystallize into CCCP, and then the bubble would be divided from the particle. Thus, we could finally get the nonspherical CCCP. Schematic diagrams of the crystallization process are shown in Figure 2, panels a–d. After solvent extraction, these Janus droplets become nonspherical photonic particles, whose shape depends on the relative volume of the bubbles. From Figure 2e, we could find that the products are of highly uniformity, reflecting bright light. Comparing the reflection spectra of colloidal crystal particle built by 200 and 260 nm PSt particles, we could recognize their unique optical reflection peak at 515 ± 5 and 650 ± 5 nm (Figure 2f), which match the theoretical calculation exactly. From the SEM images of the particles (Figure 2, panels g–i), we could observe the

meniscus has a perfect bowl-like look. When we focus on the details on the surface, we could find that the colloidal particles packing orderly and uniformly, which ensures the optical properties of the whole meniscus. With octanol as the extractant, we could finish an extraction process of a $40\ \mu\text{m}$ CCCP in no more than 15 min, similar to our previous work.

By adjusting the structure of Janus droplets, we could control the shape of colloidal microparticles. In Figure 3, panels (a–i), we can see four typical shapes, as platelike, bowl-like, potato-like, and spherical, respectively. All of them have a smooth shape and bright reflection of certain wavelengths. When we investigate the reflection spectra of CCCPs of different shapes, we could find that the relative strength of the reflection peak increases remarkably with the decrease of sphericity of microparticles (Figure 3m). It shows that the nonspherical CCCPs have stronger optical properties than the spherical CCCPs. There is a noteworthy phenomenon that the area where the curve radius is the smallest, namely the initial triphase interface, always has the best optical property, the relative area of which is positive to the integral optical properties. These phenomena accords to our initial proposed idea. So, we could control the particles' optical properties simply by adjusting the structure of Janus droplets. We compare the best CCCPs produced in this work with the best ones produced in our previous work, in Figure 3n, and find

that the platelike particles reflection peak is far stronger than that of sphere beads, which means that the integral optical properties of CCCP are greatly optimized in this work.

We proposed a possible mechanism for this phenomenon. As the extraction process only happens on one side of the aqueous droplet (the water–octanol interface), while the other side has no obvious mass-transfer, there would be circumfluence inside the aqueous phase. This phenomena is much similar to the so-called “coffee ring” effect. As a result, the partial concentration of colloidal particles around the triphase interface would be higher compared with the other part of the aqueous droplets. The high concentration decreases the possibility for colloidal particles absorbed on the interface, increasing the stability of the forced absorption of colloidal particles on the interface, and consequently improve the 2D self-assembly quality. Detailed derivation has been shown in our last work. So, in this view, the packing quality around the triphase interface would be much better, then the integral optical properties are improved. An experiment to support this mechanism is designed (see Figure S3 for the Supporting Information).

In summary, we proposed a novel method to optimize and control the optical properties of uniform CCCPs by forming uniform G-W/O Janus emulsion in a double coaxial microfluidic device, and then created a strong extraction area on the aqueous colloidal suspension droplets to enhance the self-assembly quality, partially because of the coffee ring effect. By an adjustment of the three-phase flow rate, the size and structure of the Janus droplets could be easily controlled, and then the shape of nonspherical CCCPs and the strength of CCCPs’ reflection peak could also be controlled. Compared with earlier works, we could not only give solutions to form uniform CCCPs and accomplish fabrication in a short time but also give the solution to optimize and control the optical properties. This progress could be useful in optimizing the performance of biosensors and in developing other fields related to photonic crystals.

■ 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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■ REFERENCES

(1) (a) Kim, S. H.; Park, H. S.; Choi, J. H.; Shim, J. W.; Yang, S. M. Integration of colloidal photonic crystals toward miniaturized spectrometers. *Adv. Mater.* **2010**, *22* (9), 946–950. (b) Shim, T. S.; Kim, S. H.; Sim, J. Y.; Lim, J. M.; Yang, S. M. Dynamic modulation of

photonic bandgaps in crystalline colloidal arrays under electric field. *Adv. Mater.* **2010**, *22* (40), 4494–4498. (c) Zhang, J.; Sun, Z.; Yang, B. Self-assembly of photonic crystals from polymer colloids. *Curr. Opin. Colloid Interface Sci.* **2009**, *14* (2), 103–114.

(2) (a) Sun, C.; Zhao, X. W.; Zhao, Y. J.; Zhu, R.; Gu, Z. Z. Fabrication of colloidal crystal beads by a drop-breaking technique and their application as bioassays. *Small* **2008**, *4* (5), 592–596. (b) Zhao, X.; Cao, Y.; Ito, F.; Chen, H. H.; Nagai, K.; Zhao, Y. H.; Gu, Z. Z. Colloidal crystal beads as supports for biomolecular screening. *Angew. Chem., Int. Ed.* **2006**, *45* (41), 6835–6838.

(3) Yu, Z.; Chen, L.; Chen, S. Uniform fluorescent photonic crystal supraballs generated from nanocrystal-loaded hydrogel microspheres. *J. Mater. Chem.* **2010**, *20* (29), 6182.

(4) (a) Zhendong, L.; Yangcheng, L.; Bodong, Y.; Guangsheng, L. Free Radical Polymerization of Butyl Acrylate in Monodispersed Droplets: Comparison Between Two Heating Strategies. *J. Appl. Polym. Sci.* **2013**, *127* (1), 628–635. (b) Xu, J. H.; Li, S. W.; Tostado, C.; Lan, W. J.; Luo, G. S. Preparation of monodispersed chitosan microspheres and in situ encapsulation of BSA in a co-axial microfluidic device. *Biomed. Microdevices* **2009**, *11*, 243–249. (c) Chung, S. E.; Park, W.; Shin, S.; Lee, S. A.; Kwon, S. Guided and fluidic self-assembly of microstructures using railed microfluidic channels. *Nat. Mater.* **2008**, *7* (7), 581–587. (d) Kim, S.-H.; Kim, J. W.; Kim, D.-H.; Han, S.-H.; Weitz, D. A. Enhanced-throughput production of polymersomes using a parallelized capillary microfluidic device. *Microfluid. Nanofluid.* **2012**, *14* (3–4), 509–514. (e) Kuehne, A. J.; Weitz, D. A. Highly monodisperse conjugated polymer particles synthesized with drop-based microfluidics. *Chem. Commun.* **2011**, *47* (45), 12379–12381. (f) Liu, L.; Wang, W.; Ju, X.-J.; Xie, R.; Chu, L.-Y. Smart thermo-triggered squirting capsules for nanoparticle delivery. *Soft Matter* **2010**, *6* (16), 3759. (g) Liu, S.; Deng, R.; Li, W.; Zhu, J. Polymer Microparticles with Controllable Surface Textures Generated through Interfacial Instabilities of Emulsion Droplets. *Adv. Funct. Mater.* **2012**, *22* (8), 1692–1697. (h) Xu, J. H.; Zhao, H.; Lan, W. J.; Luo, G. S. A novel microfluidic approach for monodispersed chitosan microspheres with controllable structures. *Adv. Healthcare Mater.* **2012**, *1* (1), 106–111. (i) Zhu, C.; Xu, W.; Chen, L.; Zhang, W.; Xu, H.; Gu, Z.-Z. Magnetochromatic Microcapsule Arrays for Displays. *Adv. Funct. Mater.* **2011**, *21* (11), 2043–2048.

(5) (a) Baroud, C. N.; Willaime, H. Multiphase flows in microfluidics. *C.R. Phys.* **2004**, *5* (5), 547–555. (b) Garstecki, P.; Fuerstman, M. J.; Stone, H. A.; Whitesides, G. M. Formation of droplets and bubbles in a microfluidic T-junction-scaling and mechanism of break-up. *Lab Chip* **2006**, *6* (3), 437–446. (c) Garstecki, P.; Gitlin, I.; DiLuzio, W.; Whitesides, G. M.; Kumacheva, E.; Stone, H. A. Formation of monodisperse bubbles in a microfluidic flow-focusing device. *Appl. Phys. Lett.* **2004**, *85* (13), 2649. (d) Gunther, A.; Jensen, K. F. Multiphase microfluidics: From flow characteristics to chemical and materials synthesis. *Lab Chip* **2006**, *6* (12), 1487–1503. (e) Li, S.; Xu, J.; Wang, Y.; Luo, G. A new interfacial tension measurement method through a pore array micro-structured device. *J. Colloid Interface Sci.* **2009**, *331* (1), 127–131. (f) Vladislavjević, G. T.; Shum, H. C.; Weitz, D. A. Control over the Shell Thickness of Core/Shell Drops in Three-Phase Glass Capillary Devices. *Prog. Colloid Polym. Sci.* **2012**, *139*, 115–118. (g) Xu, J. H.; Li, S. W.; Tan, J.; Wang, Y. J.; Luo, G. S. Preparation of highly monodisperse droplet in a T-junction microfluidic device. *AIChE J.* **2006**, *52* (9), 3005–3010. (h) Xu, J. H.; Luo, G. S.; Li, S. W.; Chen, G. G. Shear force induced monodisperse droplet formation in a microfluidic device by controlling wetting properties. *Lab Chip* **2006**, *6* (1), 131–136. (i) Yang, C. H.; Huang, K. S.; Lin, Y. S.; Lu, K.; Tzeng, C. C.; Wang, E. C.; Lin, C. H.; Hsu, W. Y.; Chang, J. Y. Microfluidic assisted synthesis of multi-functional polycaprolactone microcapsules: Incorporation of CdTe quantum dots, Fe₃O₄ superparamagnetic nanoparticles and tamoxifen anti-cancer drugs. *Lab Chip* **2009**, *9*, 961–965.

(6) (a) Kim, S.-H.; Jeon, S.-J.; Jeong, W. C.; Park, H. S.; Yang, S.-M. Optofluidic Synthesis of Electroresponsive Photonic Janus Balls with Isotropic Structural Colors. *Adv. Mater.* **2008**, *20*, 4129–4134. (b) Kim, S.-H.; Lee, S. Y.; Yi, G.-R.; Pine, D. J.; Yang, S.-M.

Microwave-Assisted Self-Organization of Colloidal Particles in Confining Aqueous Droplets. *J. Am. Chem. Soc.* **2006**, *128*, 10897–10904. (c) Kim, S.-H.; Lim, J.-M.; Jeong, W. C.; Choi, D.-G.; Yang, S.-M. Patterned colloidal photonic domes and balls derived from viscous photocurable suspensions. *Adv. Mater.* **2008**, *20* (17), 3211–3217.

(d) Yu, Z.; Wang, C. F.; Ling, L.; Chen, L.; Chen, S. Triphase microfluidic-directed self-assembly: Anisotropic colloidal photonic crystal supraparticles and multicolor patterns made easy. *Angew. Chem.* **2012**, *51* (10), 2375–2378.

(7) Xu, K.; Xu, J.-H.; Lu, Y.-C.; Luo, G.-S. Extraction-derived self-organization of colloidal photonic crystal particles within confining aqueous droplets. *Cryst. Growth Des.* **2013**, *13* (2), 926–935.

(8) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. Capillary flow as the cause of ring stains from dried liquid drops. *Nature* **1997**, *389* (6653), 827–829.

(9) (a) Lan, W.; Li, S.; Xu, J.; Luo, G. A one-step microfluidic approach for controllable preparation of nanoparticle-coated patchy microparticles. *Microfluid. Nanofluid.* **2012**, *13* (3), 491–498. (b) Yin, S. N.; Wang, C. F.; Yu, Z. Y.; Wang, J.; Liu, S. S.; Chen, S. Versatile bifunctional magnetic-fluorescent responsive Janus supraballs towards the flexible bead display. *Adv. Mater.* **2011**, *23* (26), 2915–2919.

(10) Chen, R.; Dong, P. F.; Xu, J. H.; Wang, Y. D.; Luo, G. S. Controllable microfluidic production of gas-in-oil-in-water emulsions for hollow microspheres with thin polymer shells. *Lab Chip* **2012**, *12* (20), 3858–3860.