Electronic Supplementary Information:

Construction of Multifunctional Photonic Crystal Microcapsules with Tunable Shell Structures by Combining Microfluidic and Controlled Photopolymerization

Jianying Wang,¹ Yuandu Hu,¹ Renhua Deng,¹ Wenjing Xu,¹ Shanqin Liu,¹ Ruijing Liang,¹ Zhihong Nie b and Jintao Zhu a,*

¹ Hubei Key Lab of Materials Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, 430074, P. R. China
b Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742 USA

* E-mail: jtzhu@mail.hust.edu.cn, Fax: (+86) 27-8754-3632

Experimental

Materials: Ethoxylated trimethylolpropane triacrylate (ETPTA), 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur1173), Fluorescein sodium salt, Tri-n-octylphosphine, tri-n-octylphosphine oxide, poly(vinyl alcohol) (PVA, M_w=13,000-23,000g mol⁻¹, 87-89% hydrolyzed), selenium shot, dimethylzinc, Bis(trimethylsilyl) sulfide, dimethylcadmium, and mercaptoacetic acid were purchased from Sigma-Aldrich. Anhydrous ethanol, chloroform, ammonia, tetraethoxysiliane (TEOS), Anhydrous iron (III) chloride, styrene, and acrylamide (AAm) were obtained from Sinopharm Chemical Reagent Co. Ltd. All of the chemicals used were of reagent quality and used without further purification unless where noted.

Preparation of microfluidic device: The uniform emulsion droplets were prepared through a microcapillary device.¹ Briefly, one round glass capillary (World Precision
Instruments) with outer and inner diameters of 1.0 mm and 580 μm, respectively, was first tapered to achieve the orifice of ~ 50 μm by using a micropipette puller (Narishige PC-10) and a microforge (Narishige MF-900). The tapered round capillary was used for injection of inner fluid. Then, the end of the other same round capillary was heated by using the micropipette puller until the diameter was up to desirable size (~ 90-180 μm) by controlling the heating condition. The heated capillary was used as the collection tube. The two tapered capillaries were then assembled into the square capillary with an inner dimension of 1.0 mm. The distance between the two round capillaries in the square tube was adjusted to be ~ 50 μm. All of the PC microcapsules were prepared by using the collection tube with an orifice size of ~ 165 μm unless where indicated.

**Synthesis of Silica nanoparticles:** Monodisperse silica nanoparticles with different diameters were synthesized by the Stöber method.² Mercaptoacetic acid capped CdSe/ZnS quantum dots with diameter of ~ 2.5 and ~ 3.5 nm were prepared by the method described in the literature.³ Poly(acrylic acid) coated magnetic nanoparticles (Fe₃O₄, size: ~ 8 nm) were prepared by using a high-temperature solution phase hydrolysis approach according to the reported procedure.⁴ Monodisperse PS microparticles were prepared through a boiling temperature soap-free emulsion polymerization, as described in the literature.⁵

**Preparation of PC microcapsules:** Microfluidic devices were employed to generate the W/O/W double emulsions. Middle oil phase was firstly prepared. [⁶] Briefly, the formed silica nanoparticles were first washed with ethanol, and then mixed with ethoxylated trimethylolpropane triacrylate (ETPTA) and a photoinitiator (2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur1173)) at various volume fractions. The suspension was placed into an oven at 70 °C for 12 h until ethanol was removed completely. The resulting silica suspensions appeared various structural colors (Fig. S6a), which were used as the middle oil phase. To stabilize the interface between the middle oil phase and outer aqueous phase, a surfactant of poly(vinyl alcohol) (PVA, 4 wt%) was added to the outer aqueous phase. The inner aqueous
phase was water or aqueous solutions containing functional substances such as dye (Fluorescein sodium salt), quantum dots (green and yellow), Fe$_3$O$_4$ nanoparticles or hydrogel monomers (acrylamide (AAm)). As the above three fluids went through the prepared microfluidic device, the inner aqueous fluid was pumped through a tapered round capillary. The middle oil fluid flowed through the outer coaxial region in the same direction as that of the inner phase while the outer aqueous fluid flowed through the outer coaxial region from the opposite direction. Flow rates of the fluids were controlled by three syringe pumps (New Era Pump System, Inc., NE-1000). All fluids were hydrodynamically focused at the exit orifice of the inner tube and formed monodisperse W/O/W double emulsion droplets after the fluids passed through the orifice. The double emulsion droplets were collected into a glass vial containing deionized water and irradiated by a UV lamp (Uvitron International, Inc., PORTA-RAY 400) to polymerize the ETPTA monomers in the middle phase. Subsequently, the obtained PC microcapsules were rinsed three times with deionized water to remove the residual surfactant.

To make nanoporous PC microcapsules, the formed PC microcapsules were immersed in 1% HF solution for 24h for complete removal of silica nanoparticles in the PETPTA shell. The single-hole PC microcapsules were prepared by irradiating the double emulsion droplets under the UV light with different light intensity. The light intensity of UV lamp (365 nm, 18 W) can be controlled by simply adjusting the distance between the sample and light source. The hole size in the PC shell increased from ~ 10 to ~ 80 μm when the above distance increased from ~ 2 to ~ 8 cm.

**Characterization:** Formation process of the emulsion droplets was monitored by using inverted optical microscope (Olympus IX71) with a CCD camera (Pixelink, PL-B742U). The microstructures of the PC microcapsules were characterized by the optical microscope and scanning electron microscopy (SEM, Philips, XL30). Before SEM investigation, the PC microcapsules were dried in air and coated with a thin layer of Pt. The dye- or QDs-labeled PC microcapsules were characterized by the inverted microscope in epifluorescence mode, equipped with a CCD camera
(Olympus DP71). The reflection spectra of the PC microcapsules were measured using a fiber optic spectrometer (Ocean Optics Inc., USB4000) attached to an optical microscope (COIC, MA2001). The structural colors were captured by using a common digital camera or the optical microscope while the intensity of the UV lamp was tested using a UV radiation meter.
SUPPLEMENTARY FIGURES

**Fig. S1** (a-e) Optical microscopy images of the PC microcapsules prepared by varying the flow rate of the inner water phase from 90, 120, 150, 180, to 200 μL h⁻¹, respectively, while the flow rates of the middle oil phase and outer water phase are kept constant of 500 and 8000 μL h⁻¹. (f) Plots of the outer diameter (D₀), the inner diameter (Dᵢ), and the shell thickness (1/2(D₀-Dᵢ)) of PC microcapsules as a function of the flow rate of the inner water phase.
(a-e) Optical microscopy images of the PC microcapsules prepared by varying the flow rate of the outer water phase from 6, 8, 10, 12, to 16 mL h\(^{-1}\), respectively, while the flow rates of the inner water phase and middle oil phase are kept constant of 120 and 500 μL h\(^{-1}\). (f) Plots of the outer diameter (Do), the inner diameter (Di), and the shell thickness (1/2(Do-Di)) of PC microcapsules as a function of the flow rate of the outer water phase.

During the preparation, we find that the stable monodisperse double emulsion droplets with single core are closely related to the ratio of the flow rates of three phases. For example, when the flow rate of the outer fluid is fixed at 8000 μL h\(^{-1}\), the stable monodisperse double emulsion droplets and the resulting microcapsules can be prepared by controlling the ratio of flow rate of middle to inner phase into a range from 1 to 5. Otherwise, if the viscosity of the middle phase is too high, we also cannot obtain the monodisperse PC microcapsules. Thus, the ratio of flow rates of three fluids and viscosity of the middle phase play the key roles in the formation of stable monodisperse double emulsion droplets and the final microcapsules.
Fig. S3 (a, b) Optical microscopy images of the PC microcapsules prepared by changing the flow rate of middle oil phase from 100 to 200 μL h⁻¹, respectively, while the flow rates of the inner and outer water phase are kept constant of 100 and 500 μL h⁻¹. In this case, the size of orifice of the round capillary for inner fluid and collection is ~ 50 and ~ 90 μm, respectively. The employed microfluidic technique allows us to fine control the overall size of the double emulsions and the resulting microcapsules by regulating flow rates, rate ratio, and/or orifice size.
Fig. S4 Optical microscopy images of the PC microcapsules with (a) dual and (b) triple liquid cores which were prepared by changing the flow rate of middle oil phase from 300 to 400 μL h⁻¹, respectively, while the flow rates of the inner and outer water phase are kept constant of 100 and 500 μL h⁻¹. In this case, the size of orifice of the round capillary for inner fluid and collection is ~ 50 and ~ 90 μm, respectively. Consequently, PC microcapsules with dual and triple holes in the shells can also be generated through the UV light irradiation with desirable intensity.
Fig. S5 (a-c) Photographs of the PC microcapsules obtained using silica nanoparticles with different diameters (at same volume fraction of 0.15): (a) 135 nm, blue capsules; (b) 140 nm, green capsules; (c) 155 nm, red capsules. We note that the structural color, especially for the red microcapsules in (c), is more brilliant than that captured by the camera and shown here. Clearly, the microcapsules can further assembly into ordered structures, as shown in (a-c).
Fig. S6 (a) Photograph of ETPTA/silica nanoparticles suspensions at different volume fraction of silica nanoparticles with a diameter of 145 nm. (b-d) Photographs of the PC microcapsules at different volume fraction of silica nanoparticles (diameter: 145 nm): (b) 0.3, blue capsules; (c) 0.2, green capsules; (d) 0.15, red capsules.
**Fig. S7** (a, b) SEM images of the hollow PC microcapsules with single-hole structure (indicated by arrows). (c) Optical microscopy image and (d) photograph of the hollow PC microcapsules with single-hole structure. In this case, monodisperse silica nanoparticles with a diameter of 150 nm were dispersed in ETPTA monomer, forming the colloidal crystal suspension (silica volume fraction: 0.2) which was used to form double emulsion droplets. The double emulsion droplets were then irradiated under UV light with the light intensity of ~ 2.0 mW cm\(^2\), forming the single-hole PC microcapsules.
Fig. S8 (a-e) Optical microscopy images of the \textit{in-situ} photopolymerization process of double emulsion droplets with the increase of polymerization time: (a) 0; (b) 10s; (c) 40s; (d) 100s; (e) 300s. The UV point light source of the microscope was used to polymerize the monomers in the shell and placed in the left side of the double emulsion droplets for formation of the gradient light intensity from left to right. Hole formed in the shell gradually from the left line of the droplets, as indicated by arrows.
Fig. S9 (a-d) Optical microscopy images of the PC microcapsules with/without single-hole structure prepared by using the \emph{in-situ} photopolymerization on microscope. (e-h) The cross-sectional SEM images of the above PC microcapsules. In this case, the distance between the above four PC microcapsules and point light source increases gradually from 0, 300, 600, to 1000 μm, respectively. The scale bar in (a) applies to (b-d) while the scale bar in (e) applies to (f-h). In this case, monodisperse silica nanoparticles with a diameter of 140 nm were dispersed in ETPTA monomer, forming a colloidal crystal suspension (silica volume fraction: 0.15) which was used to form the double emulsion droplets.

To exploit the formation mechanism of the opening hole in the shell, the polymerization process of the double emulsion droplets was observed \emph{in-situ} by using the optical microscope (Figure S8). Owing to the point light source of the microscope providing a gradually intensity of UV light, with the increase of the polymerization time, the double emulsion droplets appeared single holes (black ring in the center of inner core) (Figure S8b-S8e). Meanwhile, the sizes of single holes also showed a gradient distribution with the distance between the light source and the droplets, which can be further confirmed by the SEM characterization (Figure S9), indicating that the intensity of UV light is closely related to the hole size—the weaker the UV light intensity, the larger the hole size. The results also revealed that size of the PC microcapsules obtained is smaller than their initial double emulsion droplets while size of the inner liquid core is kept constant. Therefore, we can conclude that shell layer of double emulsion droplets occurred to shrink owing to the polymerization, which may squeeze the inner liquid core to the surface, triggering the formation of the opening hole. In summary, the single-hole formation and the hole size is closely related to the shell layer shrinkage and the curing rate induced by the light intensity.
Fig. S10 Fluorescence microscopy images (a, c) and the corresponding photographs (b, d) of the PC microcapsules containing fluorescence dye (a and b) or Quantum dots (c and d); (e) Optical microscopy image and (f) the corresponding photograph of the PC microcapsules containing magnetic nanoparticles. In this case, monodisperse silica nanoparticles with a diameter of 140 nm were dispersed in ETPTA monomer, forming a colloidal crystal suspension (silica volume fraction: 0.15) which was used as the middle phase. Aqueous solutions containing dye, QDs and magnetic nanoparticles were used as the inner phase. The obtained double emulsion droplets were then irradiated under UV light with the light intensity of above 3.5 mW cm\(^{-2}\), forming the PC microcapsules. Clearly, addition of the above three functional substances into the inner core does not influence the structural color display of the shell of the PC microcapsules.
Fig. S11 (a-c) Photographs of the magnetic PC microcapsules dispersion before (a) and after (b) its placement to a 1.3T permanent magnet for 30s. In the magnetic field, the microcapsules became magnetized, aggregated into one another, and were captured by the magnet (indicated by arrows). (c) Photograph shows that magnet in (b) was removed and the sample vial was turned 90°. The magnetic PC microcapsules were formed from the double emulsions containing the ETPTA shell with a silica (diameter: 140 nm) volume fraction of 0.15 and the aqueous inner core with magnetic nanoparticles followed by the UV irradiation with light intensity of above 3.5 mW cm⁻².
Fig. S12 Fluorescence microscopy (a-c) and optical microscopy (d-f) images of the single-hole PC microcapsules with a PAAm hydrogel inner core immersed from water, then to ethanol, and back to water.

We note that PAAm hydrogel can swell in water while deswell in ethanol. Clearly, reversible response of the inner hydrogel core from swelling to shrinking was observed when the capsules were immersed in water and ethanol, respectively. The response process of inner hydrogel core is indicated by the red circles, which suggests that the single hole in the shell provides an efficient channel to communicate with the external media.
**SUPPLEMENTARY MOVIE:**

**Movie S1:** Real-time movie shows that the PC microcapsules containing magnetic nanoparticles in their inner cores respond to external magnetic fields when the permanent magnet is applied and removed.

**REFERENCES**


