Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Separation-cooperated Assembly of Liquid Photonic Crystals from Polydisperse Particles

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S1. Experimental Section

S1.1 Chemicals and Materials

Ammonium hydroxide (28%), tetraethylorthosilicate (TEOS, 98%), dimethyl formamide (DMF, 99%) and dimethyl sulfoxide (DMSO, 99%) were purchased from Alfa Aesar (MA, USA). Acetone (99.5%), methanol (99.9%), formic acid (98%), acetic acid (99%) and anhydrous ethanol (99.5%) were from Beijing Chemical Work (Beijing, China), and acetonitrile (99.9%) was from Fisher Chemical. Capillary was purchased from Reafine Chromatography (Hebei, China). All chemicals and reagents were used as received, without further purification. Deionized (DI) water was purified by Milli-Q water filtration system (Millipore, Milford, MA, USA).

S1.2 Synthesis of silica particles

Uniform silica spheres were synthesized by a modified Stöber method (Table S1).[1] Briefly, an appropriate volume of TEOS was dissolved in ethanol, magnetically stirred for 1 hour at room temperature and rapidly mixed with another 1-h-stirred solution of ammonia in ethanol and water. The mixed solution was allowed to react for 10h to form round particles. The resulted particles were collected by centrifugation and cleaned by ethanol and water in sequence until pH 7.0. The cleaned particles were well characterized (Figure S1) and re-suspended in deionized water at 10% (w/v) for long term storage.

Table S1. Recipes for synthesis of differently sized silica particles.

Solution 1		Solution 2			Diameter
H_2O	EtOH	$NH_3.H_2O$	TEOS	EtOH	
6.3 mL	50 mL	5 mL	6 mL	50 mL	185 nm
20 mL	66 mL	14 mL	2 mL	98 mL	232 nm
20 mL	66 mL	14 mL	3 mL	97 mL	270 nm
20 mL	66 mL	14 mL	7 mL	93 mL	291 nm
24.75 mL	16.25 mL	6 mL	4.5 mL	45.5 mL	360 nm

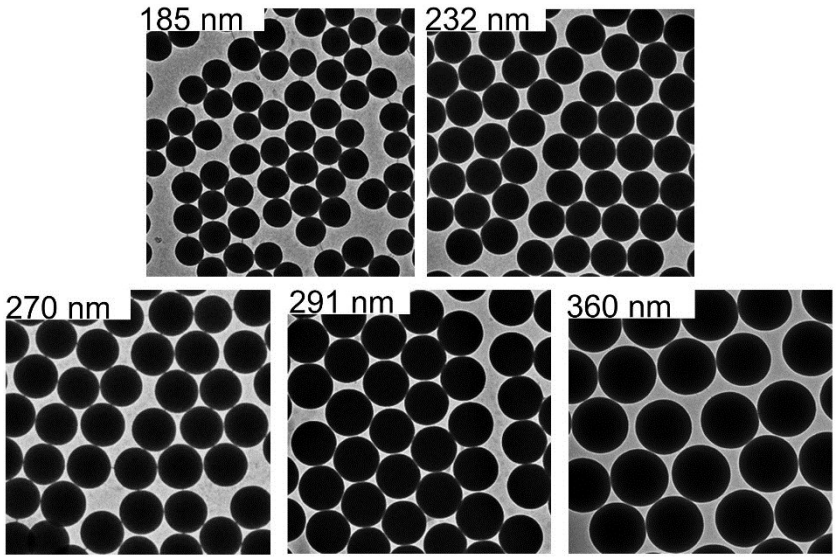

Figure S1. TEM images of laboratory-synthesized silica spheres. The diameter and the standard deviation (averaged by measuring the diameters of two-hundred silica spheres) were 185±9 nm, 232±11 nm, 270±14 nm, 291±15 nm, and 360±18 nm, respectively.

Polydisperse silica nanospheres were prepared via a titration method to control the hydrolysis and condensation of TEOS in a mixed medium of ammonia, alcohol and water.[2] For example, anhydrous ethanol (100 mL), DI water (50 mL) and ammonia (7 mL) were mixed in a round-bottomed flask through magnetic stirring at 500 rpm. For different degree of dispersion, TEOS (3mL) were added 3 or 4 times through a peristaltic pump. After reaction for 12h, silica particles with CV of 30% and 40% (Figure S2) were collected, cleaned and re-suspended in DI water for a long time of storage.

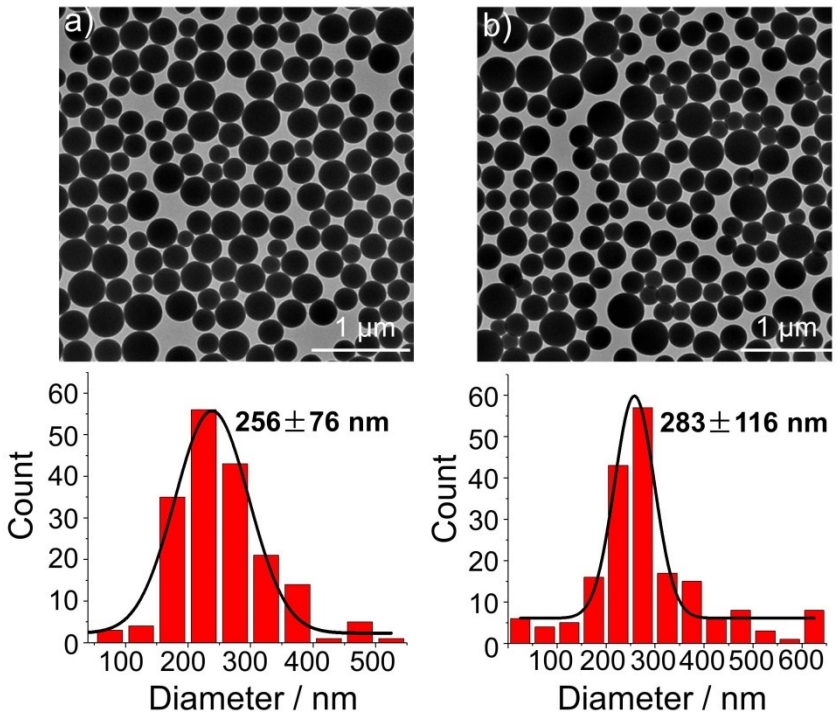

Figure S2. TEM images and size distribution of polydisperse silica particles with size CV of (a) 30% and (b) 40%, prepared by chemical synthesis.

S1.3 Synthesis of polydisperse particles of ZnO, Fe_3O_4 and TiO_2

Polydisperse ZnO spheres were synthesized by the hydrolysis of zinc acetate dehydrate (ZnAc)[3]. The reaction procedure contained two steps: preparation and growth of ZnO seed. Briefly, 2.2 g ZnAc·$2H_2O$ was added to 100 ml diethylene glycol and mixed solution was heated to 160 °C, refluxing 1h to form ZnO seed. Then taking 14 mL seed into the same ZnAc solution as first step after temperature reached 140 °C, the growth of seed was stirred for one hour. The synthetic particles were collected by centrifugation and cleaned by ethanol and water. The preparation of nonuniform Fe_3O_4 and TiO_2 was referred to literature.[4, 5]

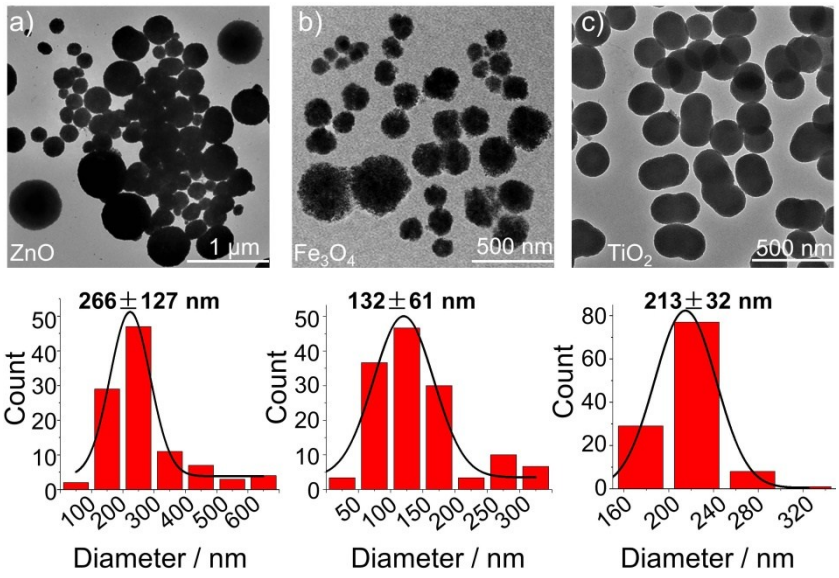

Figure S3. TEM images and size distribution of polydisperse particles as ZnO, Fe_3O_4 and TiO_2 with size CV of (a) 48%, (b) 46% and (c) 16%, prepared by chemical synthesis.

S1.4 Separation-cooperated assembly of particles into PCs

Gaussian-dispersed particles were obtained by physical mixing of 5 types of silica spheres at different diameters theoretically calculated at the required CV value. For instance, for Gaussian-dispersed particles at size center of 270 nm with CV=26%, particles of 360 nm (13.8 mg), 291 nm (15.1 mg), 270 nm (12.5 mg), 232 nm (6.7 mg) and 185 nm (1.9 mg) were mixed according to Table S2. The mixed particles were then dispersed into polar solvents such as ethanol, water, methanol, formic acid, acetone, or others, at a volume ratio (v/v) of 0.03−0.2. Similarly, the disperse particles of SiO_2, ZnO, Fe_3O_4 and TiO_2 were also chemically synthesized at CV=30%-40%, 48%, 46% and 16%, respectively, and re-suspended in methanol at a volume ratio of 0.03. For SCA, all the suspensions were separately filled in a 50-μL covered glass tube and vertically placed in a clean environment at room temperature without interference, until an iridescent zone was visible in natural light.

S1.5 Measurement of optical reflection spectra from particle suspensions

The sinking induced SCA of polydisperse particles would accomplish in 3 days or more, then the particles in a target zone were collected into a clean centrifuge tube by discarding the Inter-zonal particles to avoid size-interference. The harvested particles were washed twice with ethanol, dried by nitrogen gas stream and re-suspended into ethanol (or other solvents like methanol or water) at volume ratios of 0.2, 0.3 or 0.4, respectively. To maintain measuring conditions, an aliquot of 10 μl of the suspension was dropped on a clean glass slide and

sandwiched with another glass slide. It was then subjected to measurement of optical reflection spectra by use of a fiber spectrometer, model Ocean Optics USB4000-VIS–NIR spectrometer from Ocean Optics Co. (USA). Note: the reflection spectra of as suspension can also be measured *in situ* in a tube, in this case, all the tubes and glass slides must be carefully cleaned to get rid of the influence of dust particles.

S1.6 Preparation of PCs patterns, letters and characters

SCA-produced silica particles at a center diameter of 150 nm, 190 nm, 203 nm and 240 nm were separately suspended in water containing 5% (v/v) DMF at a volume concentration of 0.3, 0.1, 0.55 and 0.45, respectively. The first two particle suspensions were slowly filled into a 3D-printed Tai Ji model, one by one, to shape PC picture; while the latter two were separately used to write English letters or Chinese characters. All the PC-patterned picture, letters and characters were naturally dried in a clean box at room temperature.

S1.7 Determination of particle size and assembly structure

All the particle size was obtained from TEM images by averaging the measured diameter over 200 particles. To take the TEM images, a dilute particle suspension was directly deposited on a copper grid coated with formvar and a carbon layer (EMS Corp., USA) and further subjected to TEM measurement on a JEM-1011 instrument at 100 kV (JEOL Co., Japan). The assembled structure of liquid PCs was observed via a Cryo-electron microscopy of JEM-2010 instrument (JEOL Co., Japan) and dried PCs was obtained by the same equipment, just removing the freeze procedure.

S1.8 Other Instruments

All the laboratory-synthesized particles were washed by an Allegra 64R high speed centrifuge (Beckman Co., USA) and weighed by an AL104 electronic balance (METTLER Co., China). A viscometer of LVDV-II+PMPA.S (BROOKFIELD Co., USA) was used to measure the viscosity of liquids. An EOS 80D camera (Canon INC., Japan) with macro lens (EF 100mm 1:2.8L) was used to take optical digital photos. And a 3D printer, model FORM2 from Formlabs (USA) was used to fabricate the models of Chinese Tai Ji.

S2. Supplementary Discussion

S2.1 Construction of Gaussian dispersed model particles

The Gaussian-distributed model particles were artificially constructed based on the Gauss equation (Eq. S1) where x denotes the diameter of a particle sample, μ is the central size of the distributed particles and σ the standard deviation of the size.

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right) \quad \text{(S1)}$$

By this equation in combination with a designed CV, the probability of a component monodisperse particle at a giving size, *f*(*x*), can be calculated and in turn, its mass is available by (N❿ *f*(*x*)❿m) where N is the total particle number of a whole distribution, m is the averaged mass of a target particle. Considering a weighing error of 0.1 mg, the CV of a target particle size larger than 56% will become quite flat (Table S2 and Figure S4). Thus the Gaussian dispersed particles can be cut at a CV up to about 0.56 (Figure S4).

Table S2. Calculated mass of component particles to prepare Gaussian-distributed model particles at different CV values.

Component particle	Gaussian particles at size variation of					
	16%	**26%**	**46%**	**56%**	**66%**	**76%**
360 nm	5.4 mg	13.8 mg	18.8 mg	19.6 mg	20.3 mg	20.3 mg
291 nm	19.6 mg	15.1 mg	12.5 mg	12.1 mg	11.8 mg	11.7 mg
270 nm	17.1 mg	12.5 mg	10.1 mg	9.7 mg	9.5 mg	9.3 mg
232 nm	7.1 mg	6.7 mg	6.1 mg	5.9 mg	5.9 mg	5.8 mg
185 nm	0.7 mg	1.9 mg	2.5 mg	2.6 mg	2.7 mg	2.7 mg

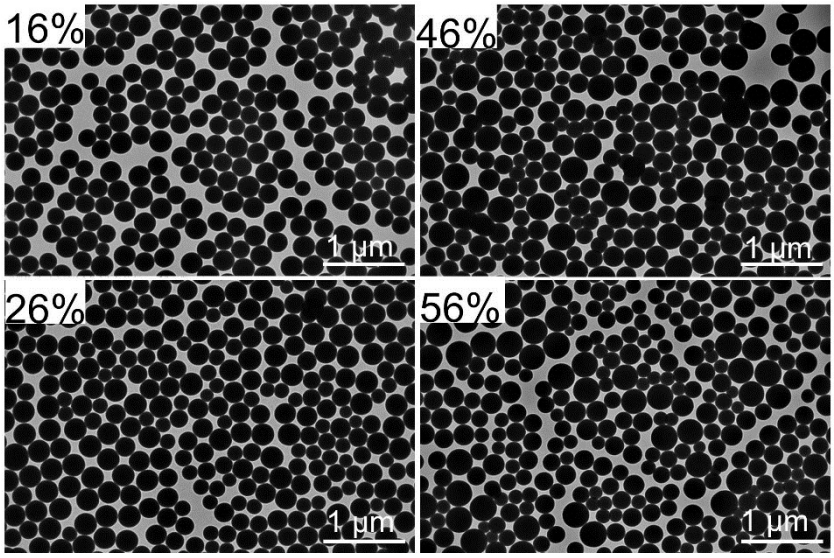

Figure S4. TEM images of polydisperse silica particles with CV ranging from 16% to 56% prepared by physical mixing according to Gauss equation.

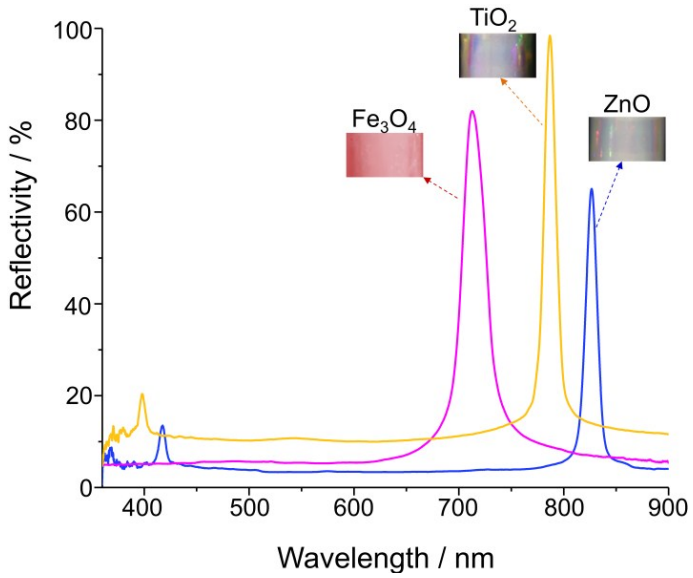

Figure S5. Digital pictures and reflection spectra from SCA-separated PC zones of polydisperse particles as ZnO, Fe_3O_4 and TiO_2 formed in methanol.

S2.2 Size-dependence of sinking speed of particles in a suspension

The sinking speed of ploydisperse particles is dependent on their size and can be calculated by a modified Stokes' equation[6, 7] (Eq. S2), where v is the sinking speed of a spherical particle with a diameter of d, Δρ is the density difference between the particle and solvent, g is the acceleration of gravity, η is the dynamic viscosity of the suspension, ϕ is the volume fraction at the very beginning, and the superscript n is determined by the Reynolds number and the diameter ratio of particle over sinking tube, commonly ranging from 4.6 to 5.5. Scott [8] suggested

that the most appropriate value of *n* is 4.7 which we adopted in the calculation. Figure S6 illustrates the cases of particles in methanol, water and ethanol.

$$v = \frac{\Delta \rho g d^2}{18\eta}(1-\Phi)^n \quad \text{(S2)}$$

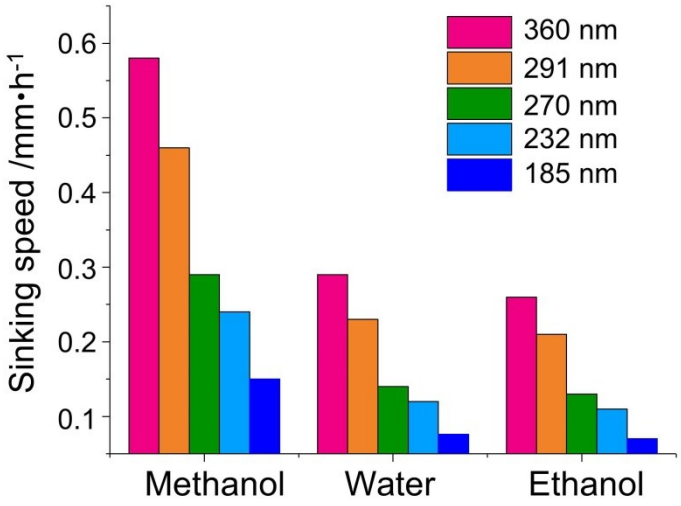

Figure S6. Sinking speed of particles at different size suspended in different solvents calculated by Eq. S2.

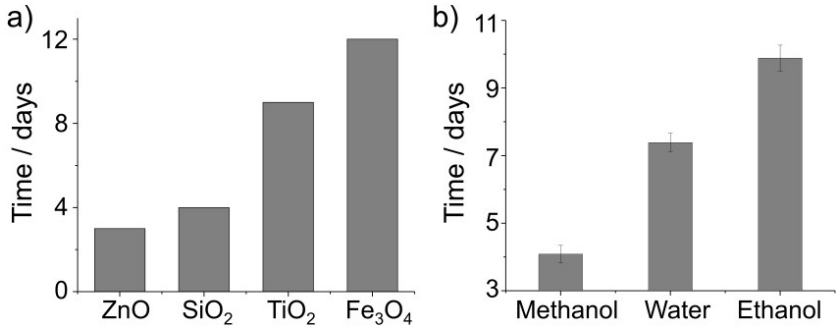

Figure S7. Sink-induced SCA time of liquid PCs from (a) polydisperse particles as ZnO, SiO_2, TiO_2 and Fe_3O_4 suspended in methanol and (b) synthesized polydisperse silica particles (CV=30%) suspended in different solvents.

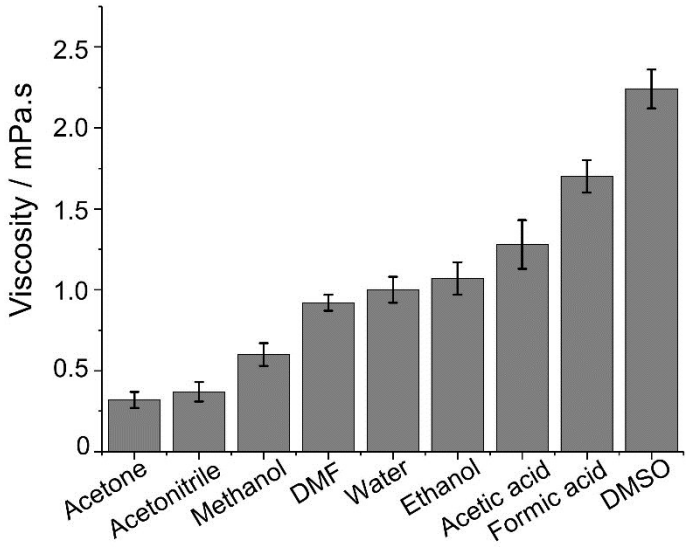

Figure S8. The viscosity of the used solvents in SCA of polydisperse silica particles.

Table S3. Optical peak height reflected from sinking induced SCA of physically mixed silica particles (CV=26%)

Solvent	Gaussian particles at volume concentration of						
	3%	**6%**	**8%**	**12%**	**13%**	**16%**	**20%**
DMF	0.16*	0.16	0.16	0.17	0.18	0.19	0.16
Acetone	0.10	0.13	0.14	0.12	0.11	0.13	0.14
DMSO	0.19	0.19	0.18	0.18	0.17	0.19	0.19
Acetonitrile	0.16	0.17	0.18	0.19	0.18	0.17	0.16
Acetic acid	0.19	0.19	0.18	0.16	0.18	0.19	0.18
Formic acid	0.18	0.17	0.16	0.18	0.16	0.15	0.16

* A total reflection was set to equal 1.00.

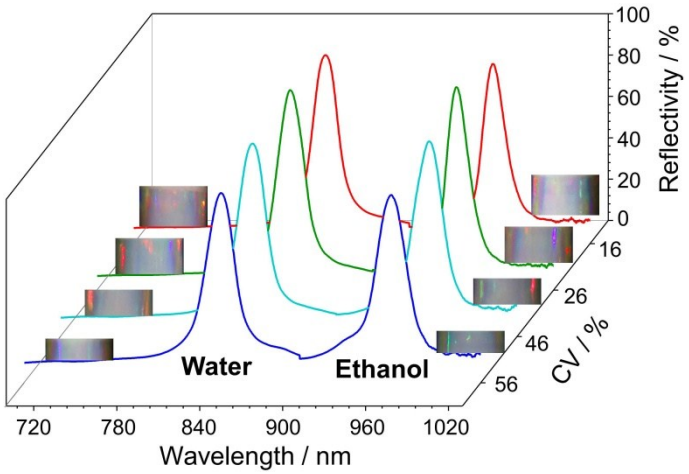

Figure S9. Digital pictures and reflection spectra from SCA-separated PC zones formed in water and ethanol, respectively.

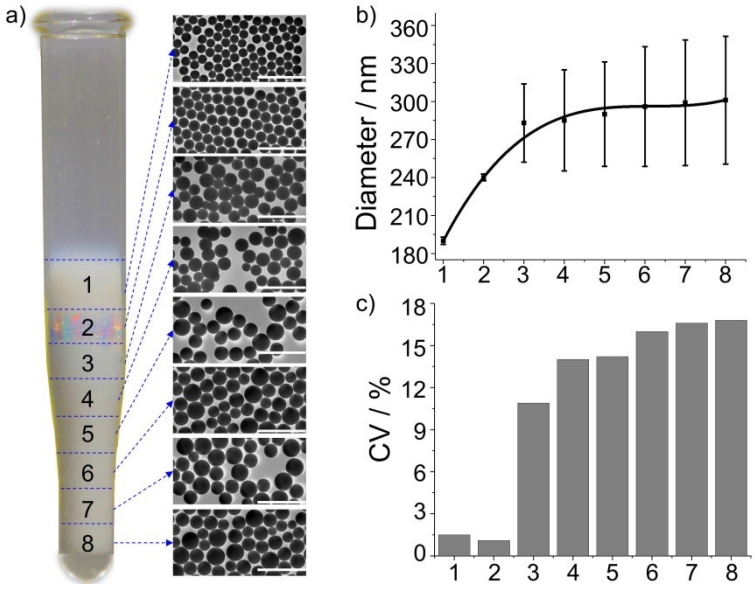

Figure S10. (a) Digital photo of SCA-produced PCs and TEM images of fractionated particles from polydisperse silica particles of CV at 0.46. (b) Corresponding size distribution and (c) size CV from position of 1-8. The scale bar is 1 μm.

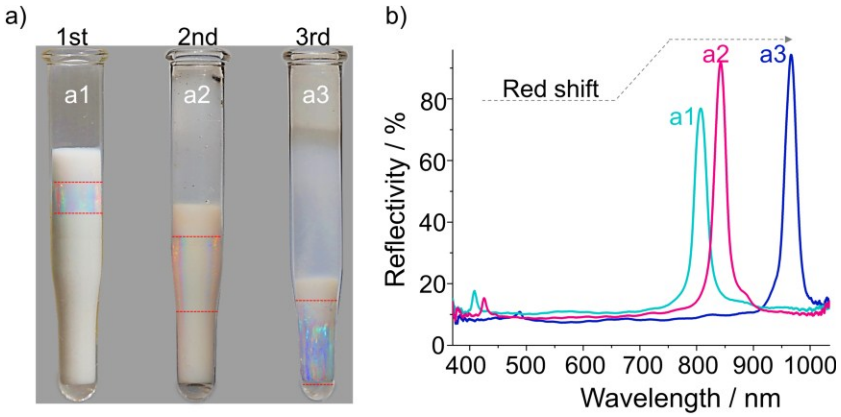

Figure S11. Digital photos (a) of sinking induced SCA of liquid PCs from synthesized silica particles with CV of 30% after 1st, 2nd and 3rd separation assembly in methanol and (b) corresponding reflection spectra. a1, a2 and a3 represents 1st, 2nd and 3rd SCA process.

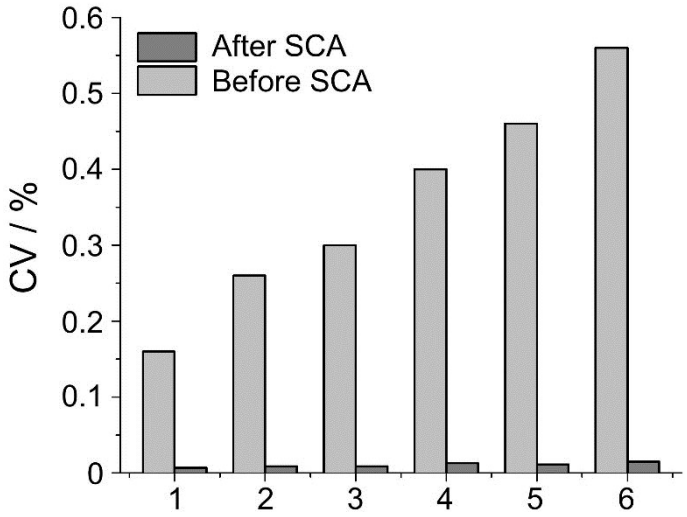

Figure S12. SCA-induced size-unification of either the Gaussian dispersed (1, 2, 3, 6) or the as-synthesized particles (4, 5).

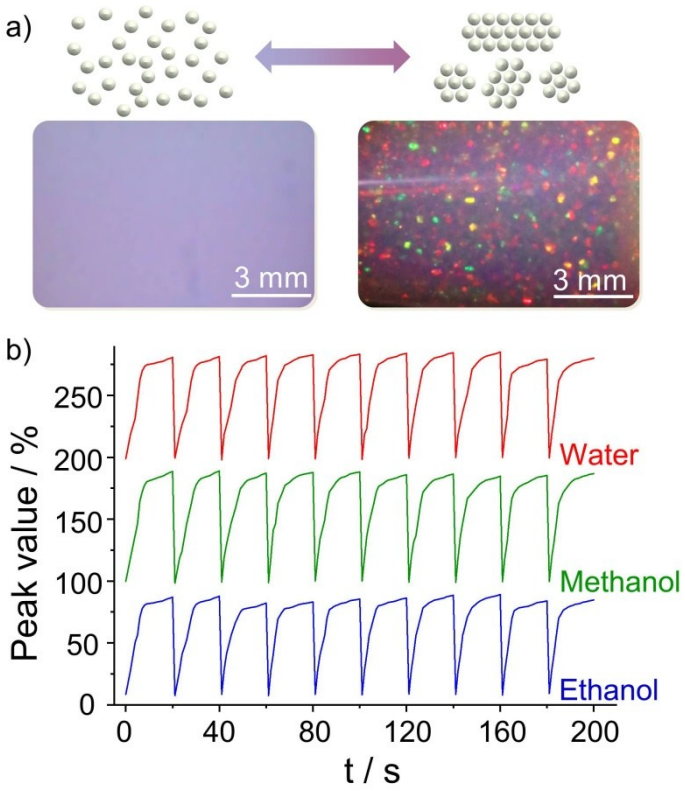

Figure S13. (a) Schematic illustrations (upper) and digital photos (lower) of reversible transformation between disordered particle suspension (left) and liquid PCs (right) in water at 40% (v/v) silica particles. (b) Cyclic variation of optical reflection intensity from liquid PCs by suspension of 240 nm SiO_2 particles at a volume concentration of 40% in ethanol, methanol and water, respectively, through alternative agitation and standing.

Table S4. Calculated distance (D_{cal}) and measured distance (D_{mea}) between neighboring particles of ordered hexagonal structures from Chinese Tai Ji pattern.

	n_{eff}	λ / nm	D_{cal} / nm	D_{SiO2} / nm	D_{mea} / nm
Liquid PCs	1.37	440	196	150	192
Dried PCs	1.34	346	158	150	151

The center to center distances between neighboring particles (D) is calculated by Eq. S3.[9]

$$m\lambda = 1.633 D n_{eff} \quad \text{(S3)}$$

$$n_{eff} = n_{SiO2}\phi_{SiO2} + n_{H20}\phi_{H2O} \text{ (**Liquid PCs**)} \quad \text{(S4)}$$

$$n_{eff} = n_{SiO2}\phi_{SiO2} + n_{air}\phi_{air} \text{ (**Dried PCs**)} \quad \text{(S5)}$$

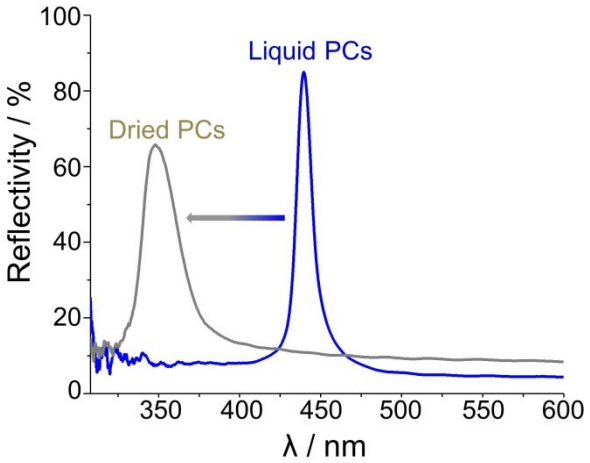

Figure S14. Reflection spectra of Chinese Tai Ji pattern before and after dryness.

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