Supplementary information

Free-standing photonic glasses with controlled disorder fabricated in a centrifugal field

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Experimental section

Materials and preparation methods:

Monodisperse, negatively charged polystyrene (PS) latex spheres were synthesized by emulsifier-free emulsion polymerization[1] and purified by dialysis against MiliQ water. 0.18 M $CaCl_2$ (>90%, Merck) aqueous solution was prepared and used as stock electrolyte. For zeta potential, dynamic light scattering and analytical ultracentrifugation measurements, diluted polystyrene and $CaCl_2$ mixtures were used. DLVO calculations were obtained using the Hamaker software package[2]. $CaCl_2$ aqueous solutions were added to concentrated (10% w.t.%) polystyrene dispersions to investigate the aggregation of the particles via scanning electron microscopy. To fabricate a free-standing monolith with glassy colloidal packing, a hydrogel precursor with a composition of acrylamide (>99%, Acros), N, N'-Methylenebisacylamide (>99%, Sigma Aldrich) and water (MiliQ) was used. Firstly, the hydrogel precursor, polystyrene dispersions and certain amount of $CaCl_2$ were mixed in a centrifuge tube (detailed parameters see table S1) and centrifuged with the L-70 ultracentrifuge (Beckman instruments, Inc.) using the Beckman swing out rotor SW 55 Ti.

Table S1.

	Monolith in figure. 5a	Monolith in figure. 5b
$CaCl_2$ aqueous solution / (0.18 M)	0.02	0.04
Aqueous acrylamide solution (40% w.t. %) / ml	0.18	0.18
Aqueous N, N'-Methylenebisacylamide solution (2% w.t.%) / ml	0.16	0.16
MilliQ water /ml	0.04	0.02
Polystyrene suspensions (10% w.t.%) / ml	0.4	0.4

Polyallomer centrifuge tubes (Beckman instruments, Inc.) were used and all centrifuge experiments were run at small centrifugal force F = 120 g to avoid possible quenching by centrifugal force. The centrifugation process was kept at a temperature of 298 K. After the centrifugation, a polystyrene-polyacrylamide composite was obtained in-situ inside the centrifuge tube by adding 0.01 ml N,N,N', N'-Tetramethylethane-1,2-diamine (>99%, Sigma Aldrich) and 0.01 ml 10% w.t. ammonium persulfate (>98%, Sigma Aldrich). The polystyrene-polyacrylamide composite can be cut into the desired shape and dried to obtain the monolith which is suitable for optical measurements.

Characterizations:

A Malvern Zetasizer Nano (Malvern Instruments Ltd.) was used to perform dynamic light scattering and zeta potential measurements. Scanning electron microscope (SEM) images were acquired using a Zeiss 249 CrossBeam 1540XB scanning electron microscope. A Beckman Optima XL-I analytical ultracentrifuge (Beckman-Coulter) was used to measure the sedimentation coefficient of the polystyrene spheres. All the AUC measurements were performed at 298 K with 6 mm thick Ti cells. Interference optics were used. The data obtained from AUC measurements were evaluated with the public domain software Sedfit (version 14.6e). The g*(s) analysis has been used to transform data derived from dc/dt to the sedimentation coefficient distribution. Asymmetrical Flow Field Flow Fractionation (AF4) measurements were conducted with a Wyatt Eclipse Dualtec control unit operating an Agilent Infintiy 1260 pump. A Wyatt "short Channel" (SC) (L = 174 mm, b_0= 24 mm, b_L= 4mm) equipped with a Nadir Regenerated Cellulose membrane (5 kDa cut-off) was used. A 0.1 % (w/v) solution of SDS and Millipore water was used as eluent. For all measurements a crossflow of V_c = 1.5 ml/min was applied. The effective channel height was determined by a reference measurement of a 200 nm PS spherical standard (Duke Scientific Corporation.). Samples were detected by a chain of a light scattering (Wyatt Dawn Heleos 8+), UV/Vis (Agilent Infinity 1100 DAD-SL) and refractive index (Agilent Infinity 1260) detector. Data evaluation was used using an inhouse processing software for AF4 data. The signal of the light scattering detector at a 27° angle was chosen to determine the hydrodynamic radii of the single fractions. Time of flight measurements were conducted in the same way as described elsewhere[2]. A laser fs-pulse is shot on the free standing samples (sample image see Figure S6a). The multiple scattered photons are collected in transmission with a time-resolved photomultiplier detection system.

Figure S1. Conventional methods to characterize the stability of nanoparticles. Zeta potential of polystyrene colloidal dispersions with different concentrations of $CaCl_2$.

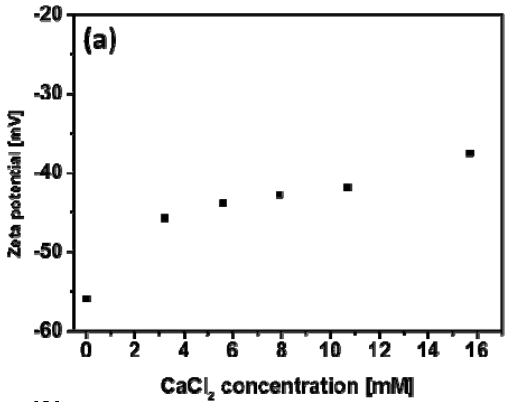


Figure S2.AF4 investigation of the sample with 11.3 mM $CaCl_2$

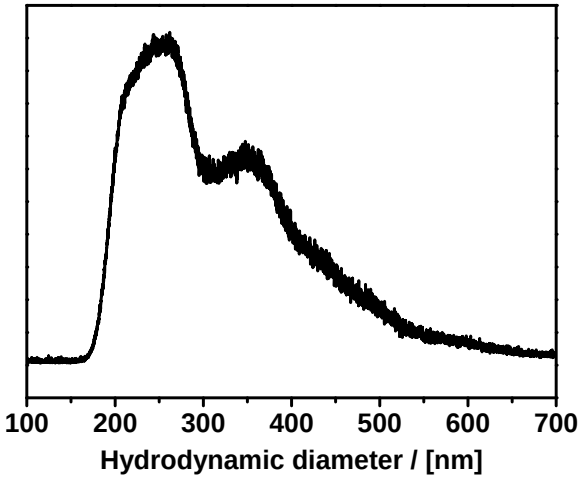


Figure S3. SEM images of colloidal glassy nanostructure prepared in a centrifugal field in presence of 5.3mM $CaCl_2$ (zoom out image of Figure 3a).

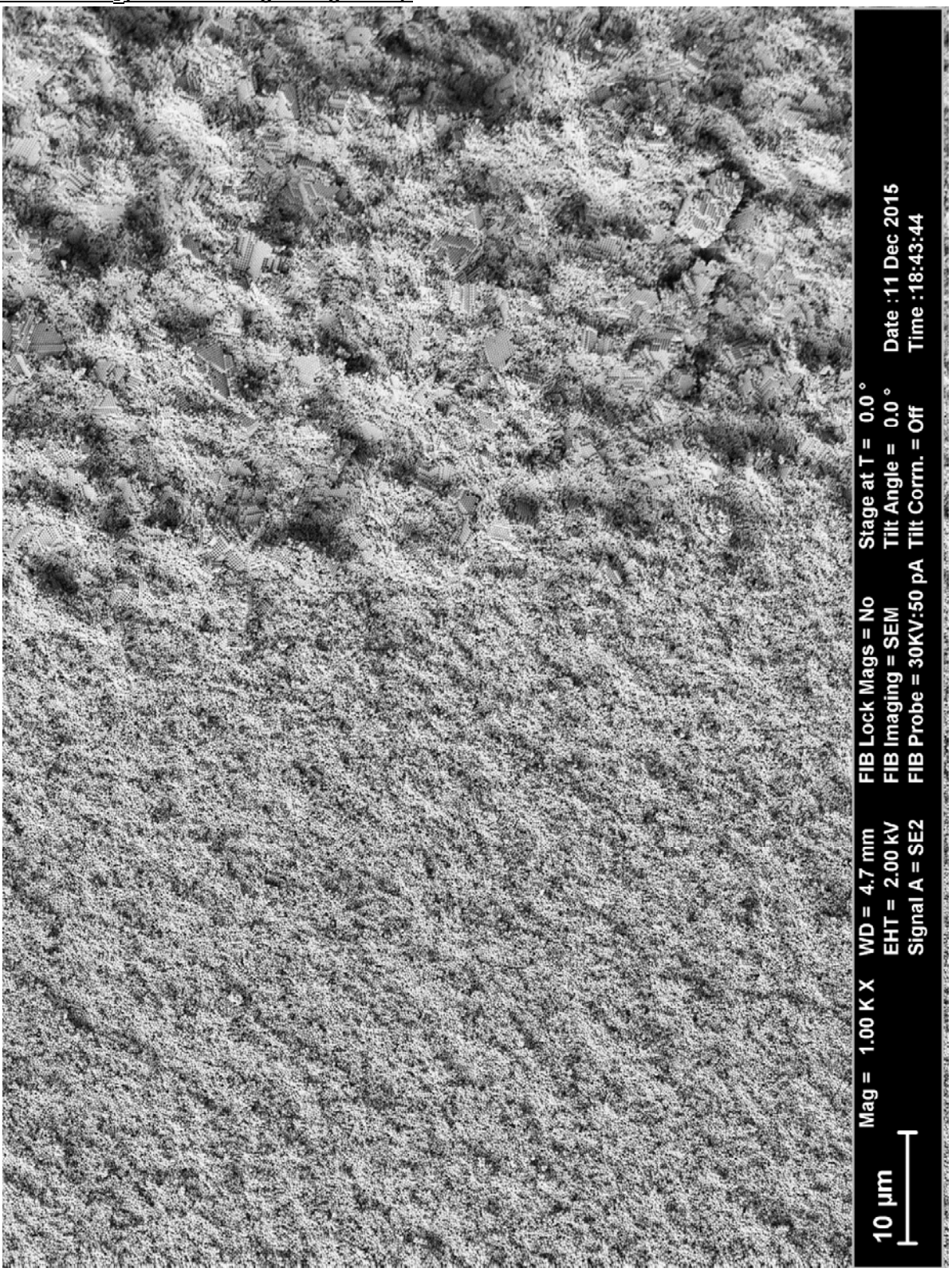
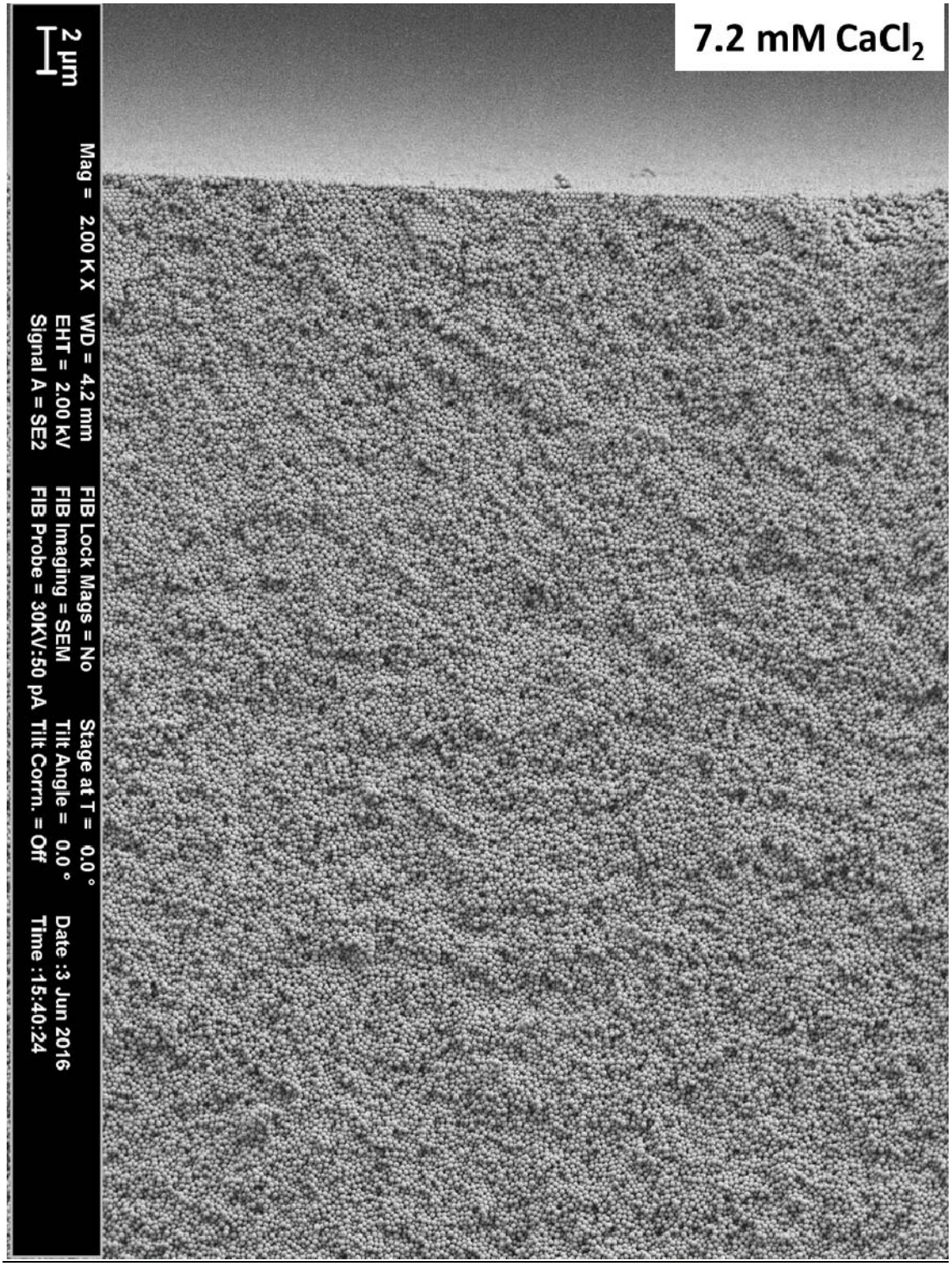


Figure S4. SEM images of colloidal glassy nanostructure prepared in centrifugal field in presence of 7.2mM and 10.1 mM $CaCl_2$.



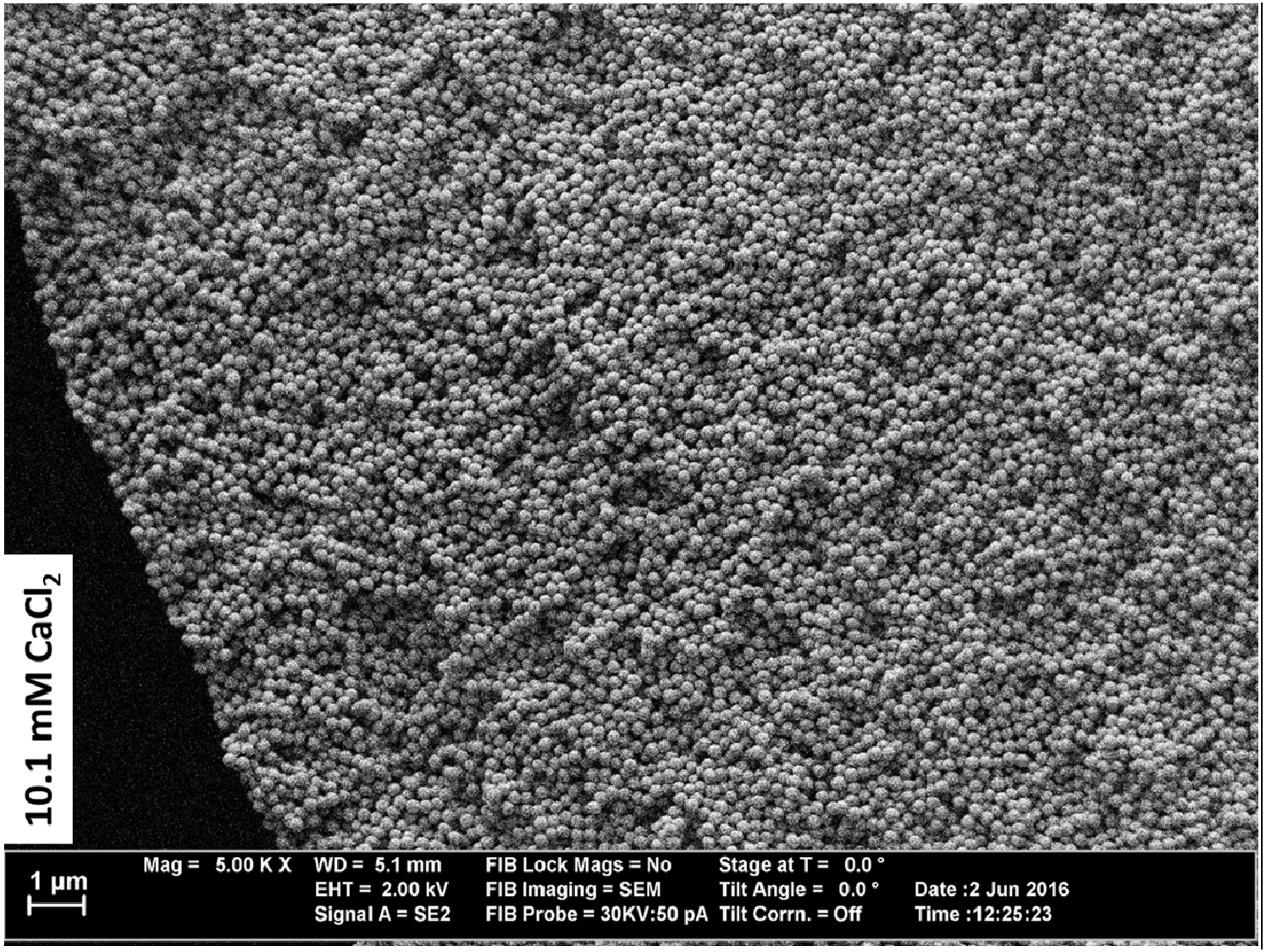

10.1 mM $CaCl_2$
1 µm
Mag = 5.00 K X
WD = 5.1 mm
EHT = 2.00 kV
Signal A = SE2
FIB Lock Mags = No
FIB Imaging = SEM
FIB Probe = 30KV:50 pA
Stage at T = 0.0 °
Tilt Angle = 0.0 °
Tilt Corrn. = Off
Date :2 Jun 2016
Time :12:25:23

Fig. S5. Image of centrifuge tube (Ultra-Clear ^{TM} 5*41 mm) and polyacrylamide hydrogel prepared inside the centrifuge tube.

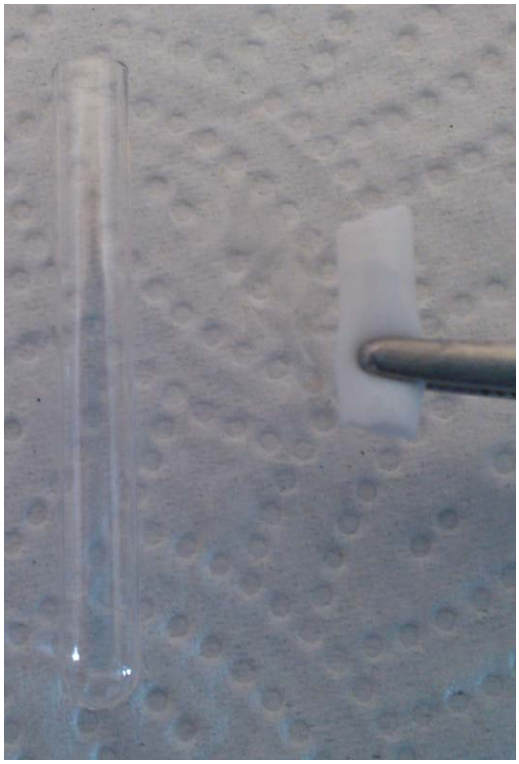
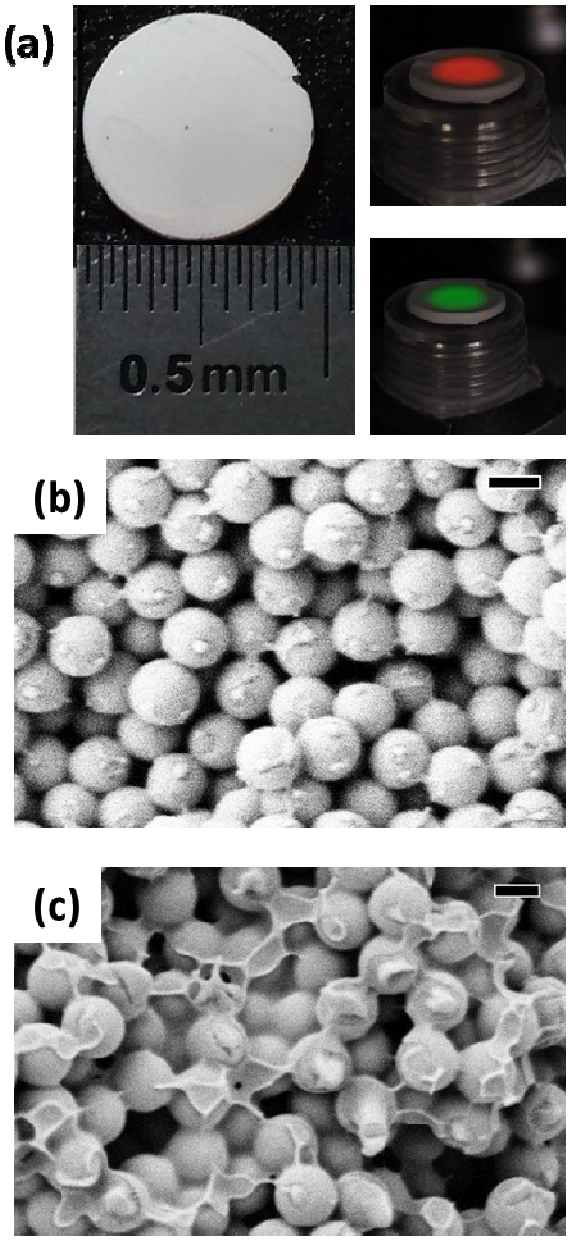


Figure S6. Polystyrene colloidal structures trapped by polyacrylamide hydrogel. (a) Images of the monolithic samples; (b) glassy structure prepared by adding low amount of $CaCl_2$ (5.3 mM); (c) glassy structure prepared by adding high amount of $CaCl_2$ (16 mM). Scale bar 200 nm.



References:

1. C. E. Reese, C. D. Guerrero, J. M. Weissman, K. Lee and S. A. Asher, *Journal of colloid and interface science*, 2000, **232**, 76-80.
2. U. Aschauer, O. Burgos-Montes, R. Moreno and P. Bowen, *Journal of Dispersion Science and Technology*, 2011, **32**, 470-479.