Supporting Information

Highly Stretchable Photonic Crystal Hydrogels for Sensitive Mechanochromic Sensor and Direct Ink Writing

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Figure S1. The particle size distribution of PBA spheres in aqueous solution before and after the swelling with EHA, determined by light scattering.



Figure S2. Fourier transform infrared spectra of ACG-12-28, AM (acrylamide) monomer, swollen PBA spheres and EHA (2-ethylhexyl acrylate) monomer. The dashed line indicates the peaks referring to unsaturated double bonds (990 cm⁻¹ for AM and 985 cm⁻¹ for EHA). The disappearance of the unsaturated double bonds in ACG-12-38 indicates the complete polymerization of the hydrophilic and oleophilic monomers.



Figure S3. Optical microscope images and reflectance spectra of CCAs. Reflectance spectra of CCAs in (a₁) water, (b₁) water/AM precursor solution and (c₁) ACGs. Optical microscope images of CCAs in (a₂-a₅) water, (b₂-b₅) water/AM precursor solution and (c₂-c₅) ACGs. Scale bars, 200 μ m. The arrows in c₁ indicate the reflectance maxima of ACG-3-38 > ACG-6-38 > ACG-9-38 > ACG-12-38, among which ACG-3-38, ACG-6-38, ACG-9-38 show weak and broad reflectance peaks.



Figure S4. 2D SAXS patterns of dehydrated (a) ACG-0-38; (b) ACG-3-38; (c) ACG-6-38; (d) ACG-9-38; (e) ACG-12-38; (f) ACG-15-38. The color bars indicate the intensities of the SAXS.



Figure S5. Photographs of stretched ACG-9-38. An ACG-9-38 sample under (a) 0% stretching deformation and (b) 2900% stretching deformation.

The mechanical property of ACG is investigated by finite element modelling (COMSOL Multiphysics) based on linear elastic theory by controlling stretch rates to define the external strain tensor.

Geometry and Materials

The geometry parameters are shown in Figure S5, with the explicit values and material properties listed in Table. S1. The corresponding geometry parameters refer

to characterizations such as colloidal spheres size (determined by light scattering) and photonic crystal nanostructures (considered as body-centered cubic structure).



Figure S6. 3D Modelling Geometry Definition. The parameters are listed in

Supplementary Table S1.

Parameter	Value	Description
Macroscopic parameters		
a	2 µm	The side length of hydrogel cell
h	300 nm	The side length of hydrogel cell
LX _{unstretch}	5 cm	The thickness of hydrogel cell
LX _{stretch}	5.5 cm	The original length of tension spline samples in x direction
ρ_1	1060 kg/m ³	The stretching length of tension spline samples in x direction
υ_1	0.47	The density of colloidal spheres
E_1	1 MPa	The Poisson's ratio of colloidal spheres
ρ_2	1120 kg/m ³	The Young's modulus of colloidal spheres
υ_2	0.47	The density of hydrogel
E_2	40 kPa	The Poisson's ratio of the PAM hydrogel

 Table S1.
 Modeling parameters list.

In the solid mechanical analysis of hydrogels, the constitutive relation of linear elastic material is governed by Hoke's law as:

 $S = C: \varepsilon_{el}$

(S1)

where S is the stress tensor, C is the elasticity tensor determined by the Young's modulus, Poisson's ratio and density. ε_{el} , representing the elastic strain, is expressed by:

$$\boldsymbol{\varepsilon} = \frac{1}{2} [(\nabla \mathbf{u})^T + \nabla \mathbf{u}]$$
(S2)

where **u** is the displacement field in x direction, and $\boldsymbol{\varepsilon}$ is controlled by external strain. As the analyzed cell is considered as one part of the whole bulk material, the elastic strain $\boldsymbol{\varepsilon}$ in x directions can be determined by deformation gradient **F** as follows:

$$\varepsilon_{ext} = \frac{1}{2} \left(F_{ext} + F_{ext}^T \right) - I_d \tag{S3}$$

$$F_{ext} = diag(\lambda_1, \lambda_2, \lambda_3) \tag{S4}$$

As the whole cell is only stretched in X direction, λ_1 be expressed as:

$$\lambda_1 = \Delta X / L \tag{S5}$$

where ΔX is length variation along the stretch directions, and L is the original length.

Boundary conditions:

1. Fixed boundary condition

As the FEM model is essentially solving the displacement vector field **u** at each mesh nodes, a fixed boundary condition is applied on the left boundary of the geometry.

2. Periodic boundary condition

Considering the fact that the analyzed geometry is a cell of the whole bulk stretched in x direction, a periodic boundary condition is applied on the y direction boundaries.

$$\mathbf{u}_{dst} = \mathbf{u}_{src} \tag{S6}$$

where u_{dst} is the displacement field of destination and u_{src} is the displacement field of source.

3. Free boundary condition

Free boundary condition is the default condition means that no force nor displacement constrain is applied. A free boundary condition is applied on the z direction boundaries.

Solver Configurations

The parametric sweep function is used to evaluate the Von Mises stress distribution of ACG with different strain rate. The analysis is studied by stationary solver using each case parameter by MUMPS direct solver.



Figure S7. The finite element simulation results with Von Mises stress distribution under the strain of 100%. The Von Mises stress distribution in ACGs with concentration of swollen PBA spheres as (a) 3%, (b) 9% and (c) 15% respectively.



Figure S8. Mechanical behaviors of different control groups. (a) Typical tensile stress-strain curves of freshly prepared ACGs with different concentration of acrylamide (from 18 wt% to 38 wt%). (b) Typical tensile stress-strain curves of freshly prepared samples of ACG-12-38 (blue line), PAM hydrogel prepared with 38% AM with 0.025 mol% N,N'-methylenediacrylamide crosslinker (black line), and ACG-12-38 prepared with non-swollen PBA spheres (red line). (c) Effects of different PBA sphere sizes on the work of extension at fracture of freshly prepared ACG-12-38. (d) Typical tensile stress-strain curves of fully swollen ACGs with different PBA spheres (from 12 wt% to 21 wt%).



Figure S9. Tensile stress–strain curves and mesostructures of ACG-12-38 with destabilized colloidal system by NaCl. a) The tensile stress-strain curves and b) elongations at break of ACG-12-38 prepared with different concentration of NaCl (from 0 to 5 mM). Atomic force microscopy images of dehydrated samples of (c) ACG-12-38 and (d) ACG-12-38 prepared with 5 mM NaCl. Scale bars, 1 μm. The atomic force microscopy images indicates the agglomeration of the PBA spheres in ACG-12-38 by introduction of NaCl to the precursor solution.



Figure S10. The finite element simulation results of ACG with destabilized colloidal system. The Von Mises stress distribution in ACG with agglomerated PBA spheres (9 wt%).



Figure S11. Cyclic compressive stress–strain curves of swollen ACG-9-38. (a)Cyclic compressive stress-strain curves of swollen ACG-9-38 under strains of 20%,40%, 60%, 80%, 98% and (b) the detail view.



Figure S12. Photographs of ACG-12-38 under tensile strains. The photographs of the gel taken at different tensile strains show the shift of structural colors from 3D Bragg diffraction of red to blue-violet with gradual increase in strain, and the 2D Bragg diffraction thereafter.



Figure S13. Schematic diagram of 3D Bragg diffraction.

3D Bragg diffraction is caused by the diffraction between two adjacent crystal planes:

$$\lambda_{max} = 2d_1 \left(\sum_i n_i^2 V_i - \sin^2 \theta \right)^{\frac{1}{2}}$$
(S7)

where d_1 is the distance between two adjacent crystal planes, n and V are the refractive index and the volume fraction of each component in the CCA crystalline phase, and θ is the angle between the incident light and the sample normal.

In the case of freshly prepared ACG-12-38 with BCC crystalline structure and spherical diameter of 180 nm, the average refractive index can be calculated by

 $n_{sphere}=1.47$, $n_{PAM-hydrogels}=1.38$, $V_{sphere}=0.68\left(\frac{180}{d_2}\right)^3$, $V_{PAM-hydrogels}=1-V_{sphere}$, where d_2 is the distance between two adjacent spheres in the (110) close packed plane of BCC structure. The structural colors in Figure S12 and Figure 5a were observed under normal incident and normal observation, thus $\theta = 0$. The 3D Bragg's law can be simplified as:

$$\lambda_{max} = 2d_1 \left(\sum_i n_i^2 V_i\right)^{\frac{1}{2}} = 2\frac{\sqrt{6}}{3}d_2 \left(1.47 * 1.47 * 0.68 \left(\frac{180}{d_2}\right)^3 + 1.38 * 1.38 * (1 - 0.68 \left(\frac{180}{d_2}\right)^3)^{\frac{1}{2}}\right)^{\frac{1}{2}}$$
(S8)

As the λ_{max} (when strain=0%) in Figure 5a is 610 nm, the d₂ of ACG-12-38 is calculated to be approximately 270 nm.



Figure S14. Schematic diagram of 2D Bragg diffraction.

Under normal incident condition, the 2D diffraction follows:

$$\lambda_{max} = \mathrm{nd}_2 \mathrm{sin}\,\theta \tag{S9}$$

where d_2 is the distance between two adjacent spheres in a crystal plane. n is the refractive index of the phase where the optical path difference (Δ l) goes through. In this case, the spheres were surrounded by PAM hydrogels, so that the n refers to n_{PAM} hydrogels=1.38. θ is the angle between the normal incident light and the reflected light. In the case of freshly prepared ACG-12-38, the d₂ is approximately 270 nm as mentioned above, and the θ in Figure 5c is 40 degree, so that the λ_{max} of 2D diffraction at strain=0% is calculated to be 240 nm which is invisible. In Figure 5c, the d₂ is increased with a tensile strain of 110%, the λ_{max} of 2D diffraction is calculated to be 503 nm, very close to the measured 2D diffraction maxima in Figure 5d at 510 nm which can be observed in visible light region.



Figure S15. Atomic force microscopy images of ACG-12-38 (a) before and (b) after stretching with elongation of 200%. The arrow in b indicates the stretching direction. Scale bars, 1 μm.



Figure S16. An embossed pattern on a dehydrated ACG-12-38. Scale bar, 2 mm. The pattern was based on the ACG-12-38 compressed by a stamp followed by dehydration to fix the shape.



Figure S17. Images of dehydrated ACG-12-38 patterns. Six typical pattern images of the embossed pattern on a dehydrated ACG-12-38 by (a-f) stereoscopic microscope and (a'-f') green channels only. Scale bars: 200 μ m. The images showed the random features caused by CCA microcrystals.



Figure S18. Reversible reflectance shifts of ACG-17-31 under compression. Normal incident reflectance spectra of fully swollen ACG-17-31 (a) under uncompressed state, (b) compressive stress of 12.7 kPa, and (c) released after the compression.



Figure S19. Linear relationship between the reflectance maxima and the compressive stress of fully swollen ACG-17-31.

Table S2.	Summary of linear reflectance shifts by deformations and the full width a	t
half-maxin	um of the reflecance peaks of some reported photonic soft materials.	

	Linear range	Full width at	
Hydrogal Systems and Mathods	of reflectance	half-maximum	Reference
Hydroger Systems and Methods	shifts by	(in the initial	
	deformations	position)	
	220 nm		This work
Colloidal-array crosslinked photonic hydrogels	(communication)	~18 nm	(ACG-27-
	(compression)		23)
PAAm-PAA photonic hydrogel with macroscopic single-	300 nm	50 mm	01
domain lamellar bilayers	(compression)	~30 IIII	51
Metastable SiO ₂ colloidal crystalline array in Poly-	150 nm	10 mm	S2
(ethylene glycol)-co-poly(ethylene glycol) methacrylate	(compression)	~19 IIII	
Non-Close-Packed SiO ₂ array embedded in poly-	~140 nm	28	S3
(poly(ethylene glycol) phenyl ether acrylate)	(compression)	$\sim 28 \text{ nm}$	
Regularly arranged core-shell particles cross-linked by UV	90 nm	40	0.4
irradiation	(stretching)	~40 nm	84
PS photonic crystals embedded in poly(dimethylsiloxane)	~90 nm	~50 nm	S 5
Blue phase liquid-crystalline polymers	~ 100 nm	~19 nm	S6



Figure S20. Summary of maximal reflectance shifts and elongation at break of some reported photonic soft materials.

Table S3.	Summary of some macromolecular microsphere composite hydrogels in
fully swolle	n state.

	Tensile	Compressive		
Hydrogel Systems and Methods	Strain	Strain	Reference	
	at Fracture	at Fracture		
Colloidal array arosolinkad nhatania hydrogola	1900%	>98%	This work	
Conoidai-array crossniked photonic hydrogers			(ACG-27-23)	
In situ polymerization of an emulsion system that contained				
hydrophilic monomers of N,N-dimethylacrylamide and	2600%	85%	S13	
hydrophobic monomers of lauryl mathacrylate				
Core-shell latex particles as crosslinking centers	2000%	>90%	S14	
Starch-based nanospheres with derivable allyl groups as		0.40/	015	
nanoscale crosslinkers	-	94%	815	
Pluronic F127 diacrylate as crosslinker	1320%	-	S16	
Polyacid nanogels crosslinked PEG hydrogel	230%	96%	S17	
A polymerizable macromolecular micelle with hydrophobic	700%	>90%	S18	
cores locked by hydrogen bonds as a crosslinker				
Vinylated chitosan as a macro-crosslinker	929%	98%	S19	
Poly(acrylamide) nanocomposite hydrogels, reinforced by				
calcium hydroxide nano-spherulites in the assistance of N,N'-	2200%	97%	S20	
methylenebisacrylamide				
Lignin nanoparticles (LNP) employed as cross-linking	692%	97%	S21	
junctions				
PNIPAM activated nanogels as nano-crosslinkers	1800%	-	S22	
Two-phase composite structure, where the continuous phase is				
a loosely cross-linked polyacrylamide matrix and the disperse	1270%	-	S23	
phase is virtually double-network microgels				

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