Electronic Supplementary Material (ESI) for Materials Horizons.


# Supporting Information

# Stable, Stimuli-Responsive Anisotropic Hydrogels for Sensing Ionic Strength and Pressure

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## 1. Experimental

*General:* All compounds were used as received from Aldrich without further purification. Aqueous dispersions of cellulose nanocrystals (CNCs) were supplied from FPInnovations in acidic form (6.0 wt%, pH = 1.9), obtained by a procedure described previously.[1] The sizes and degree of sulfation are the same as the ones we have used in a recent study (384 ± 89 nm x 14 ± 14 nm; zeta potential about -30 mV); the reference includes a TEM image.[2] Thickness of the hydrogels was measured by a digital micrometer (Marathon Management Co.) using a pair of cover glasses to sandwich the hydrogel. Polarized optical microscopy images were acquired on an Olympus BX41 microscope under crossed polarizers. UV-visible spectroscopy was carried out on a Cary 5000 UV-Vis/NIR spectrophotometer using the hydrogels on glass microscope slides perpendicular to the beam path with a holder having a 10 mm diameter circular hole. SEM images were taken on a Hitachi S4700 electron microscope with sputter-coated samples (5.0 nm of Pt-Pd). 2D XRD patterns of the freeze-dried hydrogels glued to a metal post along the shear direction were collected with a Bruker APEX DUO diffractometer equipped with an APEX II CCD detector using Cu Kα1 X-ray beam with a wavelength (λ) of 0.154 nm at 0.6 mA, 45 kV for 480 s at 60 mm from the detector in transmission mode.

**Preparation of CNC hydrogels (SH1-SH6, UH4):** The aqueous CNC dispersion (10.0 g, 6.0 wt%) was heated at 80 °C with vigorous stirring, then evaporated to give a viscous dispersion (6.0 g, 10.0 wt%). A precursor for the hydrogels was prepared by mixing the 10.0 wt% CNC dispersion (6.0 g) with acrylamide (0.27 g, 3.7 mmol), N,N'-methylenebisacrylamide (14 mg, 94 μmol) and 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (2.7 mg, 12 μmol). Appropriate amounts (20, 40, 80, 120, 160, 200 mg) of the precursor were transferred to a space (12 x 25 mm) on glass microscope slides in between two spacers of cellulose acetate tape (0.05

mm thickness each) piled up to be a certain thickness (**SH1**: 0.05, **SH2**: 0.10, **SH3**: 0.20, **SH4**: 0.30, **SH5**: 0.40, **SH6**: 0.50 mm). Another microscope slide (ca. 19 x 25 mm) was pressed down on top of the space to shear the material, sliding it back and forth along the long axis in > thirty repetitions at a rate of ca.1.25 cm/s. A 300 nm ultraviolet-B light source (8 W) was used for the photopolymerization. Ultraviolet irradiation was applied for 2 h to give the sheared CNC hydrogels (**SH1**-**SH6**). An unsheared CNC hydrogel (**UH4**, thickness: 0.30 mm) was prepared by the same procedure used to make **SH4**, but without the shearing process.

*Calculation of Hermans order parameter (S)*:[3,4] From the 2D XRD patterns (Figure 1d and Figure S1), plots of the intensity (I) with respect to azimuthal angle (ϕ) were obtained by scanning along the arc defined by 2θ = 22.9°, which corresponds to the (200) reflections of the cellulose Iβ crystals. Then the combination of two equal Lorentz distributions was fit to the plots by the least-squares method to obtain the profile of I(ϕ). The order parameter, S, was calculated from I(ϕ) following the method described in the previous report using equations 1-3.

$$S = \frac{3\langle cos^2\gamma\rangle - 1}{2} \quad (1)$$

$$\langle cos^2\gamma\rangle = 1 - 2\langle cos^2\phi\rangle \quad (2)$$

$$\langle cos^2\phi\rangle = \frac{\int I(\phi)\ cos^2\phi\ \sin\phi\ d\phi}{\int I(\phi)\ \sin\phi\ d\phi} \quad (3)$$

where γ is the angle between the (200) planes and the shear direction.

*Calculation of the birefringence*:[5] The transmittance for the perpendicular ($T_\perp$) and parallel ($T_\parallel$) orientations of the analyzer relative to the polarizer are given by equations (5) and (6), where $\theta$ is the angle between the polarization axis of the polarizer and the shear direction, fixed at 45° in the measurements and δ is a phase difference between the two polarizations expressed by equation (4) where $d$ is the thickness of the sample and λ is the wavelength of light. Birefringence, $\Delta n$, in equations (7) and (8) can be derived from the combination of equations (4), (5) and (6), where $k$ is a non-negative integer that describes the order of the solution. From basic principles of these optically transparent materials, we know that $\Delta n$ is continuous across the visible spectrum. It can also be shown that the order $k$ is constant between maximum and minimum in $T_\perp / T_\parallel$. Using this information, it is therefore possible to manually choose $k$ for each set of data.

$$\delta = \frac{2\pi \Delta n\, d}{\lambda} \qquad (4)$$

$$T_\perp = \sin(2\theta)\ \sin^2\frac{\delta}{2} \qquad (5)$$

$$T_\parallel = \sin(2\theta)\ \cos^2\frac{\delta}{2} \qquad (6)$$

$$\Delta n = \frac{\lambda}{2\pi d}\left[k\pi + 2\tan^{-1}\sqrt{\frac{T_\perp}{T_\parallel}}\right] \qquad k = 0, 2, 4, \ldots \qquad (7)$$

$$\Delta n = \frac{\lambda}{2\pi d}\left[(k+1)\pi - 2\tan^{-1}\sqrt{\frac{T_\perp}{T_\parallel}}\right] \qquad k = 1, 3, 5, \ldots \qquad (8)$$

Since our hydrogels are optically transparent throughout the visible region, the refractive index can be modeled by the first-order Sellmeier dispersion: $n(\lambda)^2 - 1 = a + b\lambda^2/(\lambda^2 - \lambda_0^2)$, where $a$, $b$, and $\lambda_0$ are constants. It can be reduced to the simpler Cauchy formula: $n(\lambda) = A + B/\lambda^2$, where $A$ and $B$ are constants for a given material. The dispersion of our birefringent hydrogels is therefore modeled by the following equation (9):

$$\Delta n(\lambda) = n_e(\lambda) - n_o(\lambda) \approx \Delta n_\infty + \frac{C}{\lambda^2} \qquad (9)$$

where $\Delta n_\infty$ is the birefringence at long wavelengths and $C$ is a constant. Note that the absolute values of the ordinary ($n_o$) and extraordinary ($n_e$) indices are not required to determine $\Delta n(\lambda)$. In order to calculate the dispersion of the birefringence, we combine equations (7), (8) and (9) and use least-squares minimization to find the parameters $\Delta n_\infty$ and $C$ that give the closest fit to our experimental data.

*Swelling ratio:* Swelling ratio of the hydrogel was evaluated by measuring the length ($L$) and the width ($W$) from the image taken under crossed polarizers (50 x 50 mm) and the thickness ($d$) measured by a digital micrometer (Marathon Management Co.) using a pair of cover glasses to sandwich the hydrogel.

*Pressure sensing:* For quantification of the pressure applied to the hydrogel, we used a device in which four screws running through the center of the springs (Century Spring Corp. B14-23;

spring rate, $k$ = 0.54 N/mm) penetrate through the screw holes at every corner to tighten two aluminum plates with a hole ($\phi$10 mm) at the center as a window for optical measurements. A linear polarizer (50 x 50 mm) is fixed on the aluminum plate and a glass plate (50 x 50 mm) on another plate so that the hydrogel can be homogeneously compressed between the windows. Pressure ($P$) applied to the hydrogel placed between the polarizer and the glass plate can be quantified based on a change in the length of the springs from the initial position ($\Delta x$ (mm)) measured using digital calipers (Mastercraft®) through tightening the screws, calculated by the expression:

$$P \ \text{(kPa)} = \frac{4 \times 0.54 \ \Delta x}{A} \times 10^{-3}$$

where $A$ ($m^2$) is the contact area of the hydrogel either to the polarizer or the glass plate. The value of $A$ was estimated from the thickness ($d$), the initial thickness ($d_0$) and the initial area ($A_0$) of the hydrogel assuming that the volume doesn't change with the applied pressure:

$$A = A_0 \times \frac{d_0}{d}$$

## 2. Supporting Figures

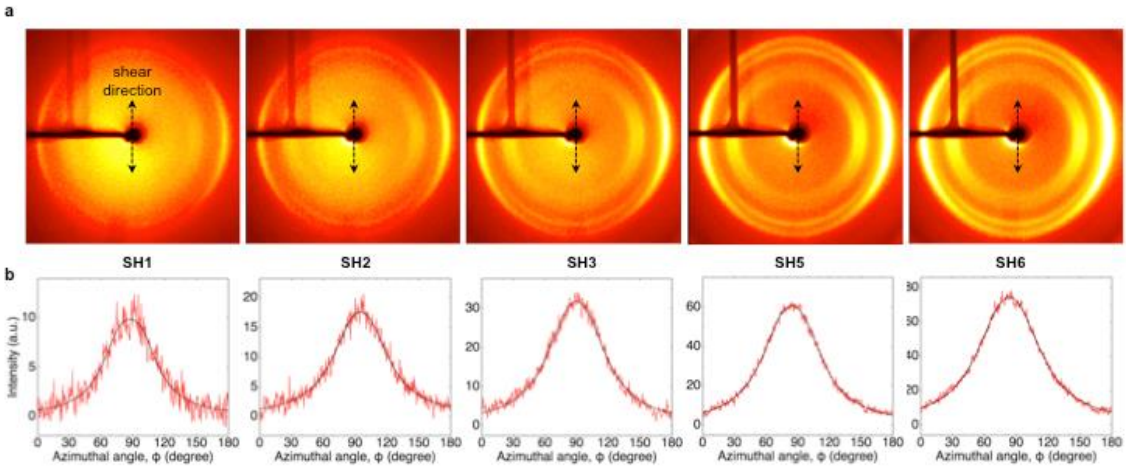


**Figure S1.** Structural characterization of the sheared CNC hydrogels (**SH1-SH3, SH5** and **SH6**). (a) 2D XRD patterns and (b) plots of the intensity with respect to azimuthal angle ($\phi$) were obtained by scanning along the arc defined by $2\theta$ = 22.9° for **SH1-SH3**, **SH5** and **SH6** showing the anisotropic distribution in diffraction intensity.

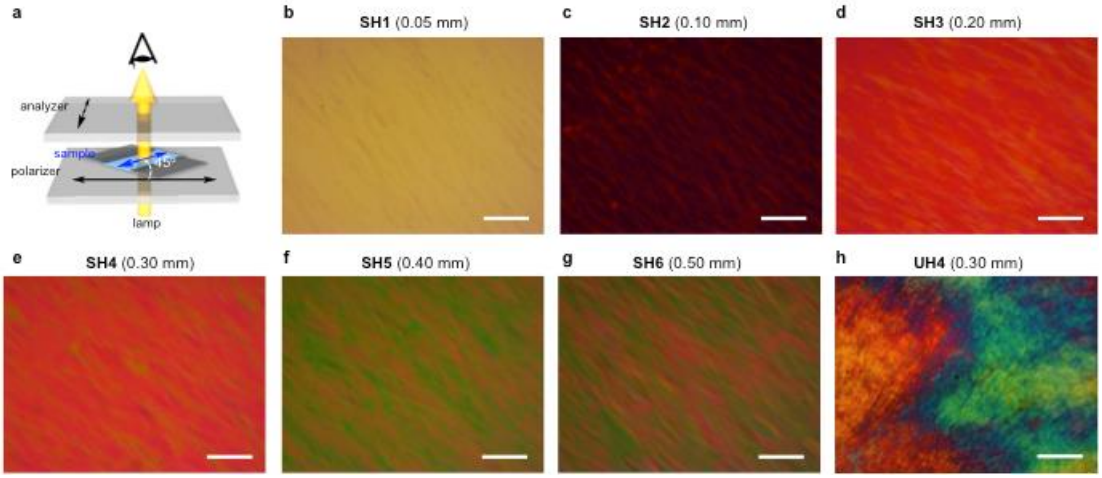


**Figure S2.** POM images of **SH1-SH6** and **UH4**. (a) The experimental setup for POM images of **SH1-SH6** placed with the shear direction at 45° with respect to the polarization axis of each of the crossed polarizers. (b)-(g) Monochrome POM images of **SH1-SH6** indicating the mono-domain anisotropic structure with unidirectional alignment of the CNCs. (h) A multicolored POM image of **UH4** demonstrates its multi-domain structure. All scale bars represent 50 μm.

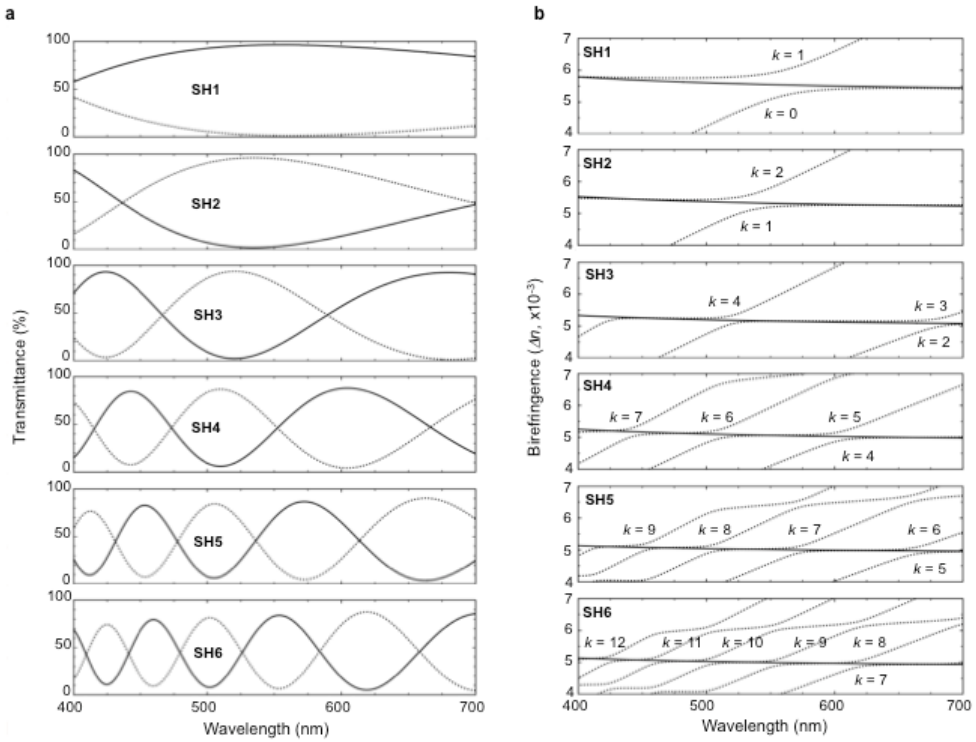


**Figure S3.** Data for the calculation of the birefringence dispersion for the sheared CNC hydrogels (**SH1**-**SH6**). (a) A pair of transmission spectra for **SH1**-**SH6** placed with the shear direction at 45° with respect to the polarization axis at 45° under crossed and parallel polarizers. (b) The birefringence dispersions calculated using equations (7), (8) with the indicated constants *k* and curves fitted using Cauchy formula, equation (9).

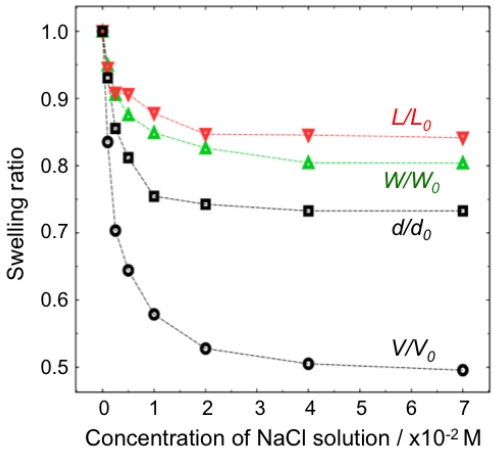


**Figure S4.** Swelling behavior of the unsheared CNC hydrogel (**UH4**). Swelling ratio ($V/V_0$, $W/W_0$, $d/d_0$ and $L/L_0$) of **UH4** with different concentrations of NaCl solution.

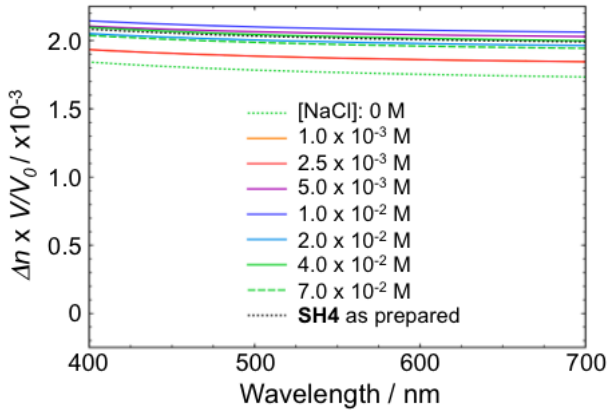


**Figure S5.** The birefringence ($\Delta n$) dispersions of **SH4** swelled in different concentrations of NaCl solution multiplied by the volume swelling ratio ($V/V_0$) to normalize the birefringence to account for the change in volume. The birefringence dispersion of **SH4** as prepared is also shown as a reference.

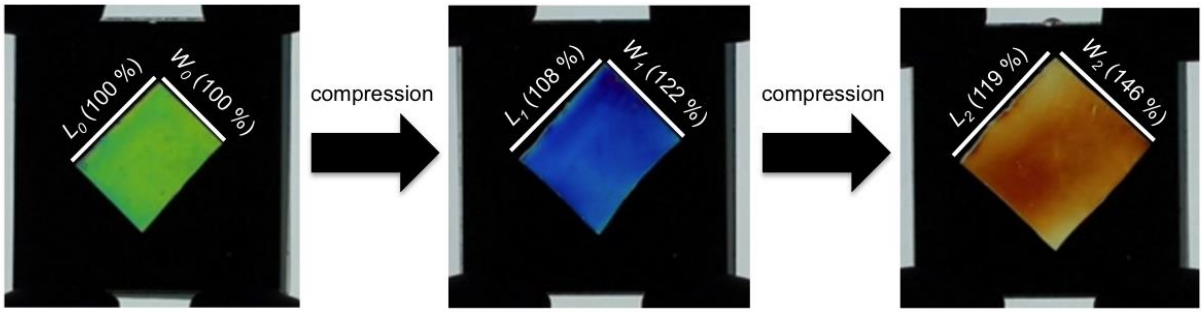


**Figure S6.** The anisotropic shape variation of the water-swelled sheared CNC hydrogel (**SH4**) throughout the compression.

# References

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