Supporting Information

Modulating the Structural Orientation of Nanocellulose Composites through Mechano-stimuli

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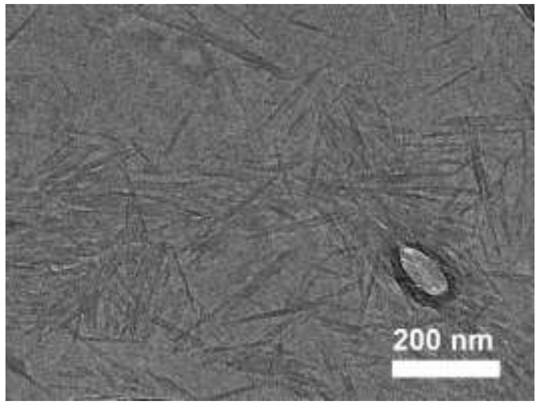

Figure S1. TEM image of CNCs nanorods in DMF suspension.

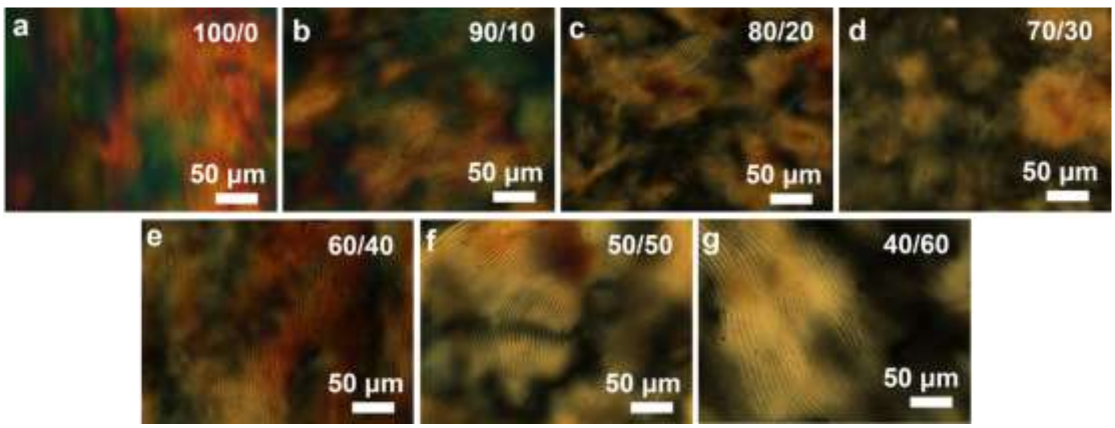

Figure S2. POM images of CNC/PU (*x/y*) suspensions with different CNC/PU weight ratios showing fingerprint texture.

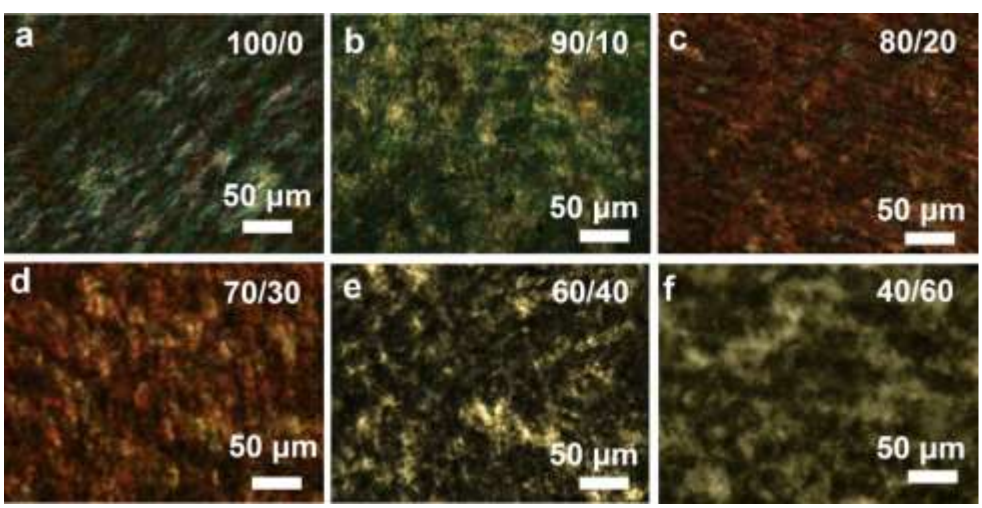

Figure S3. POM images of composite CNC/PU (*x/y*) films with different CNC/PU weight ratios showing strong birefringence.

Table S1. Thickness of CNC/PU composite films.

CNC/PU	100/0	90/10	80/20	70/30	60/40	50/50
Thickness (µm)	62±5	54±7	55±10	57±7	55±10	61±8

Surface roughness

To quantify the film surface roughness we measure, R_a which is the arithmetic mean of the absolute values of vertical deviation from the mean line through the profile. Also, R_q (RMS) was measured which is the square root of the arithmetic mean of the square of the vertical deviation from a reference line. Each measurement was repeated *in triplicate* from 4 different regions of a cast film.

$$R_a = \frac{1}{AB}\int_A^B |y|dx = 0.77\ \mu m \pm 0.11$$

$$R_q = \sqrt{\frac{1}{AB}\int_A^B y^2 dx} = 0.97\ \mu m \pm 0.08$$

R_q is greater than R_a, which may indicate a single large peak, or flaw within the microscopic surface texture raising the RMS value more than the average height value.

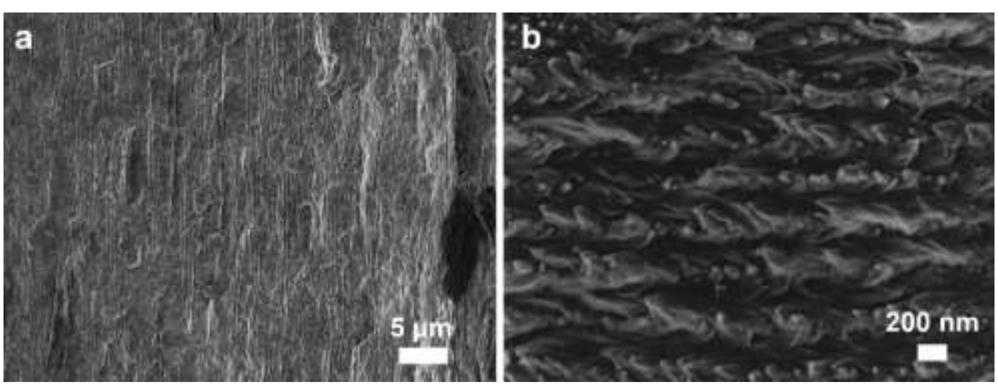

Figure S4. (a) Low and (b) high magnification SEM images of CNC/PU (40/60) film showing periodical left-handed chiral nematic arrangement.

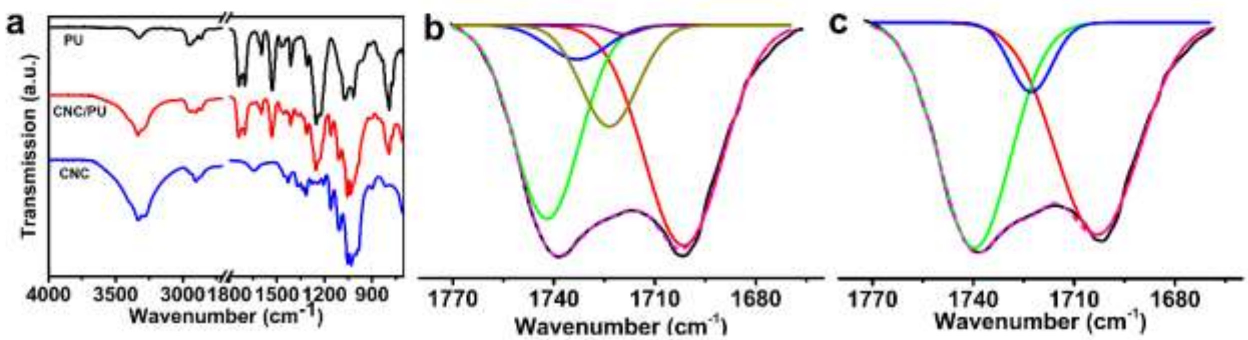

Figure S5. FTIR spectra of (a) pure CNC, pure PU and CNC/PU (50/50) composite films. In pure PU film, 3325 cm^{-1} is N-H stretching vibration, 2950 $cm^{-1}$and 2858 cm^{-1} correspond to C-H stretching bands, 1701 cm^{-1} is associated with hydrogen bonded C=O, 1741 cm^{-1} band belongs to free C=O, 1534 cm^{-1} belongs to Amide II vibration band. In pure CNC film, 3332 is O-H stretching vibration. All bands appear in CNC/PU composite film. Deconvolution of carbonyl group (C=O) in pure PU film using (b) five sub-peaks and (c) three sub-peaks.

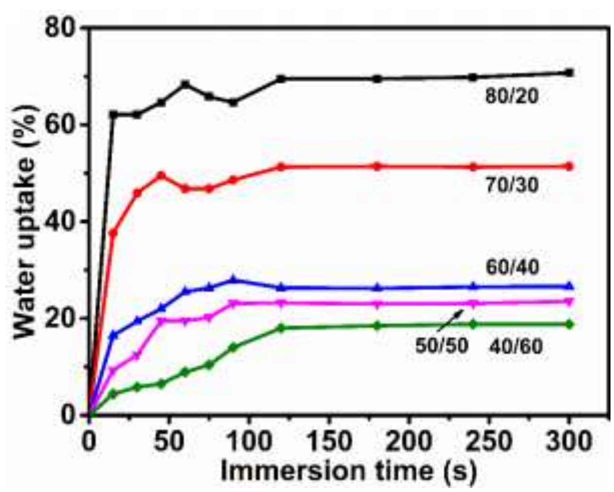

Figure S6. Water uptake of composite films with different CNC/PU weight ratios.

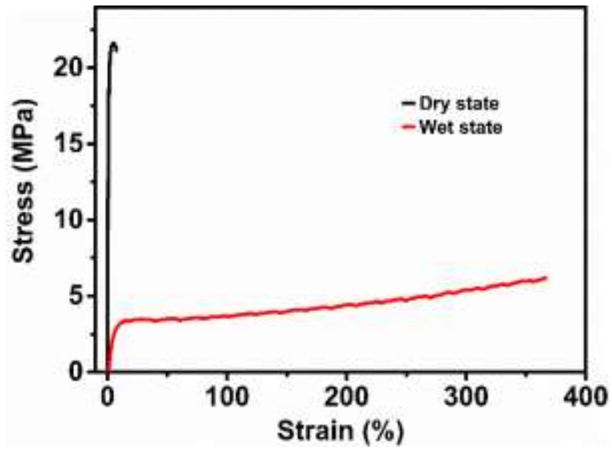

Figure S7. Stress-strain curves of CNC/PU (50/50) films in dry and wet states.

Table S2. Mechanical properties of neat PU and CNC/PU (50/50) films in dry and wet states (the elongation at break and strength of neat PU film in wet state were not shown due to the limitation of tensile machine).

	PU film		CNC/PU (50/50) film	
	Dry state	Wet state	Dry state	Wet state
Elongation at break (%)	393	-	7.5	366
Strength (MPa)	6.5	-	22	6.2
Young's modulus (MPa)	53	30	6000	50

Table S3. Recovery performance of stretched CNC/PU (50/50) films (200% elongation) in different conditions.

Recovery conditions	25 °C oven	25 °C water	75 °C oven	75 °C water	95 °C oven	95 °C water
Recovery ratio in first cycle (%)	0	39.9	0	53.4	0	53.4

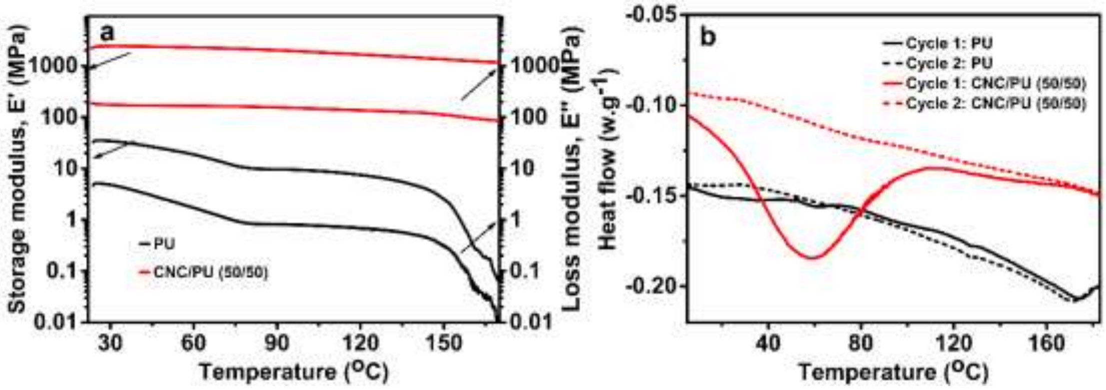

Figure S8. (a) Storage and loss moduli of neat PU and composite CNC/PU (50/50) films. (b) Two-cycles DSC curves of pure PU and composite CNC/PU (50/50) films.

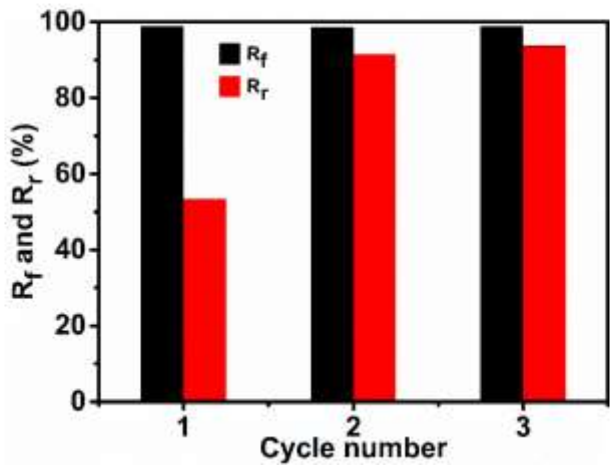

Figure S9. Shape fixation (R_f) and shape recovery ratio (R_r) of composite CNC/PU (50/50) film.

Table S4. Moduli of PU and CNC/PU (50/50) films in wet and dry states during shape memory process.

Modulus (MPa) / Cycle number	PU film		CNC/PU (50/50) film	
	Wet state	Dry state	Wet state	Dry state
1	30	53	55	6000
2	23	46	51	6300
3	24	48	40	6800

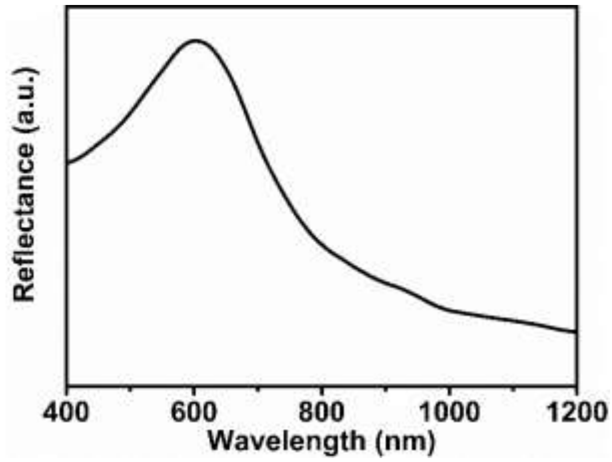

Figure S10. UV-Vis-NIR reflection spectrum of CNC/PU (50/50) film at 100% strain.

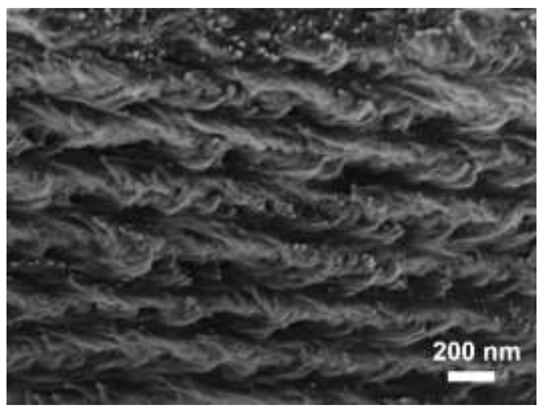

Figure S11. SEM image of CNC/PU (50/50) film at 100% strain.

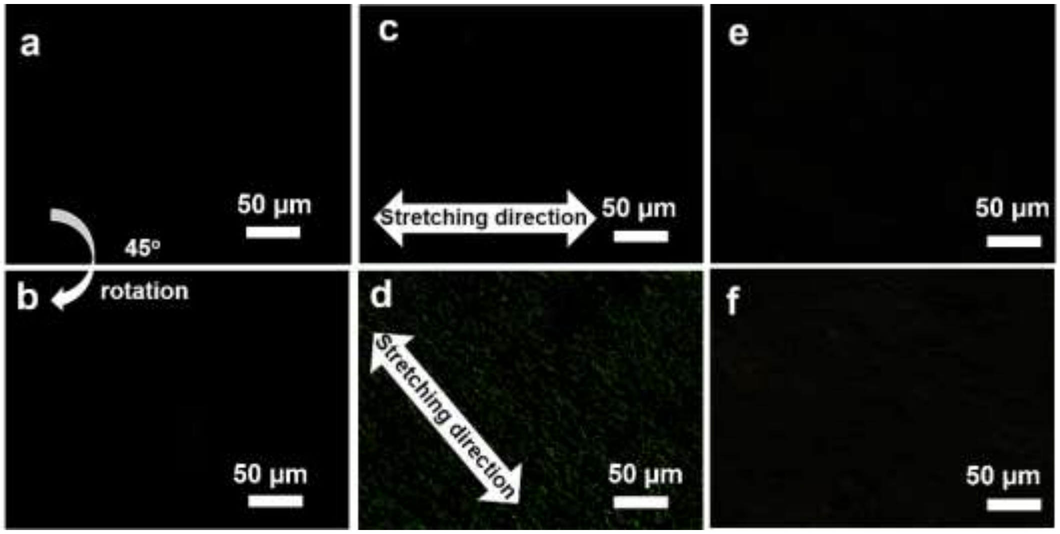

Figure S12. POM images of PU films under crossed polarizers using same exposure time with CNC/PU (50/50) film. (a,b) Initial film at 0° and 45° to the polarizers showing isotropic structure, (c,d) 200% stretched film showing dark field at 0° and weak birefringence at 45°, (e,f) the recovered film showing isotropic structure.

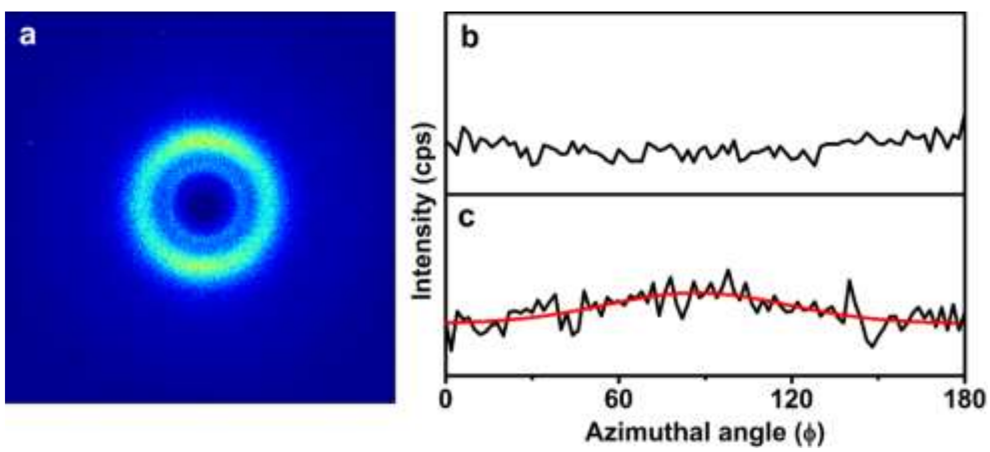

Figure S13. (a) Two-dimensional WAXS pattern, and azimuthal intensity profiles for neat PU film stretched up to strain of 200%. (b) Profile at $2\theta = 21°$-$22.3°$ showing angle-independence. (c) Profile at $2\theta = 17°$-$21°$ indicating orientation of the PU matrix.

Table S5. CNC alignment at different stages of the shape memory programming process for CNC/PU (50/50) film.

Sample	Herman order parameter (*f*)
Initial film	0.01
100% strain	0.48
200% strain	0.63
Recovered film	0.31

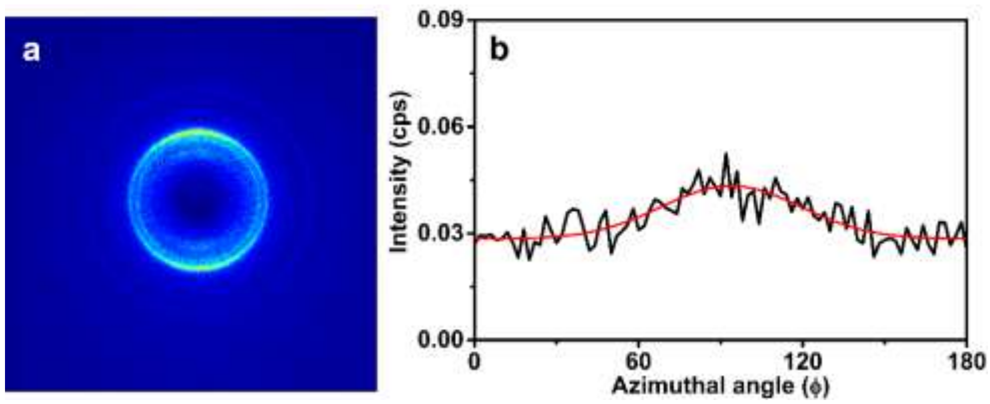

Figure S14. (a) Two-dimensional WAXS pattern and (b) azimuthal intensity profile of CNC/PU (50/50) film stretched up to strain of 100%.