Supporting Information

Liquid Behaviors-Assisted Fabrication of Multidimensional Birefringent Materials from Dynamic Hybrid Hydrogels

Heqin Huang, Xiaojie Wang, Jinchao Yu, Ye Chen, Hong Ji, Yumei Zhang, Florian Rehfeldt, Yong Wang and Kai Zhang*

Materials

Microcrystalline cellulose (MCC), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), 3-(acrylamido)phenylboronic acid (PBAAM), methacrylic anhydride, sodium hydrochloride, phosphotungstic acid hydrate, 2,4,6-trimethylbenzoyl chloride were purchased from Sigma-Aldrich (USA). Dopamine hydrochloride, dimethyl phenylphosphonite, and 2-butanone were obtained from Alfa Aesar (USA). Acrylamide (AM), sodium sulfate anhydrous, disodium tetraborate were bought from Merck Millipore (USA). Sodium hydroxide was ordered from VWR (Germany). Sodium bicarbonate was bought from TH Geyer (Germany). Hydrochloric acid (37%) was obtained from AppliChem (Germany). The organic solutions, including tetrahydrofuran (THF), ethyl acetate, nhexane, and acetone, were all purchased from TH Geyer (Germany). Deionized water utilized throughout all experiments was purified from a Millipore system. Dopamine methylacrylate¹ and lithium
phenyl-2,4,6-trimethylbenzoylphosphinate (LAP)\(^2\) were synthesized with previous reported method.

Figure S1. Dynamic hybrid hydrogels preparation with \textit{in situ} polymerization.

Figure S2. TEM image of CNC and polarized image of CNC suspension in DI water (concentration as 1.6 mg/ml).
Figure S3. Oscillation shear frequency sweep of DH1.25 and DH1.25/CNC2.

Figure S4. Shape regulation of dynamic hydrogels along the time. The edges of cubic hydrogel become round in 12 hours.
Figure S5. 3ITT shearing tests with low-high-low strain sweep of DH1.25 and DH1.25/CNC2.

Figure S6. Tensile strain-stress curves of dynamic hydrogels with various amounts of CNC.
Figure S7. The hysteresis tensile tests of DH1.25/CNC2.

Figure S8. 3ITT shearing test with low-high-low strain sweep of 6 wt% CNC suspension in pH=10 borax-NaOH buffer.
Figure S9. Stretched dynamic hydrogels with diverse amounts of CNC. The dynamic hydrogels networks show limited anisotropy, while CNC are necessary to form the interference colors in hydrogels.

Figure S10. a) Biaxial stretching of DH1.25/CNC2. b) XG1.25/CNC2 without stretching.
Figure S11. Polarizing optical microscopy images of XG1.25/CNC2.

Figure S12. Schematic explanation of laser scattering equipment.
Figure S13. 2D WAXS measurements for the characterization of the CNC alignment. (a) 2D WAXS images of XG1.25/CNC2 (P4, with $\lambda = 3, 6, 9$). (200) reflections of the cellulose I$\beta$ crystals were pointed out; (b) Azimuthal intensity profiles base on (200) reflections showing narrowing fwhm with increasing elongation ratio $\lambda$. 
Figure S14. Xerogels prepared with various crosslinks density in dynamic hydrogels. The crosslinking density of hydrogels can be tuned with the concentration of PBA/catechol complexes. The densely crosslinked dynamic hydrogels showed less contraction in width, which was in return compensated by larger contraction in depth. Therefore, even shifted interference colors were observed, the dynamic hydrogels with various crosslinking density had similar maximum birefringence in the resulted xerogels.

Figure S15. Polarizing optical microscope image of XG1.25/CNC2 W₀/D₀=1.
Figure S16. a) Polarizing optical microscope images of XG1.25/CNC2 $W_0/D_0=32$; b) the changing of birefringence along the red dash line in a); c, d, e) Semi-transparent XG1.25/CNC2 with haze properties.

Figure S17. The surface of central area of XG1.25/CNC2 $W_0/D_0=32$; left: SEM top view of the films; right: surface topography observation from LSM.
Figure S18. Anisotropic mechanical properties and fracture morphologies of XG1.25 \( W_{0}/D_{0}=32 \) and XG1.25/CNC2 \( W_{0}/D_{0}=32 \).
Figure S19. Fracture interface of XG1.25/CNC2 W/D₀=32 in the direction parallel to the CNC alignment. The wrinkled structures were formed near the fracture interface. In the zoom-in images of SEM, aligned CNC on the fracture surface can be observed. The pull-out process of CNC can effectively dissipate energy during stretching and promoted the ductile fracture.
Figure S20. Fiber shaped XG1.25/CNC2 $W_0/D_0=1.2$ with different elongation ratio.
Figure S21. Birefringence comparison of XG1.25/CNC2 tubes and corresponding XG1.25/CNC2 \( W_0/D_0=20 \) as films.

References
