Supporting Information for

Flexible and tough cellulose nanocrystal/polycaprolactone hybrid aerogel based on the strategy of macromolecule crosslinking via click chemistry

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Supporting information consists of 7 pages, 1 Table and 9 figures.

Table S1. CNC-PCL composite aerogels with different concentrations of PCL-N and volume of DMF

Sample	CNC-C	PCL-N	Vol_{DMF}
CP0.1	1	0.1	100
CP0.25	1	0.25	100
CP0.5	1	0.5	100
CP0.25-60	1	0.25	60
CP0.25-140	1	0.25	140

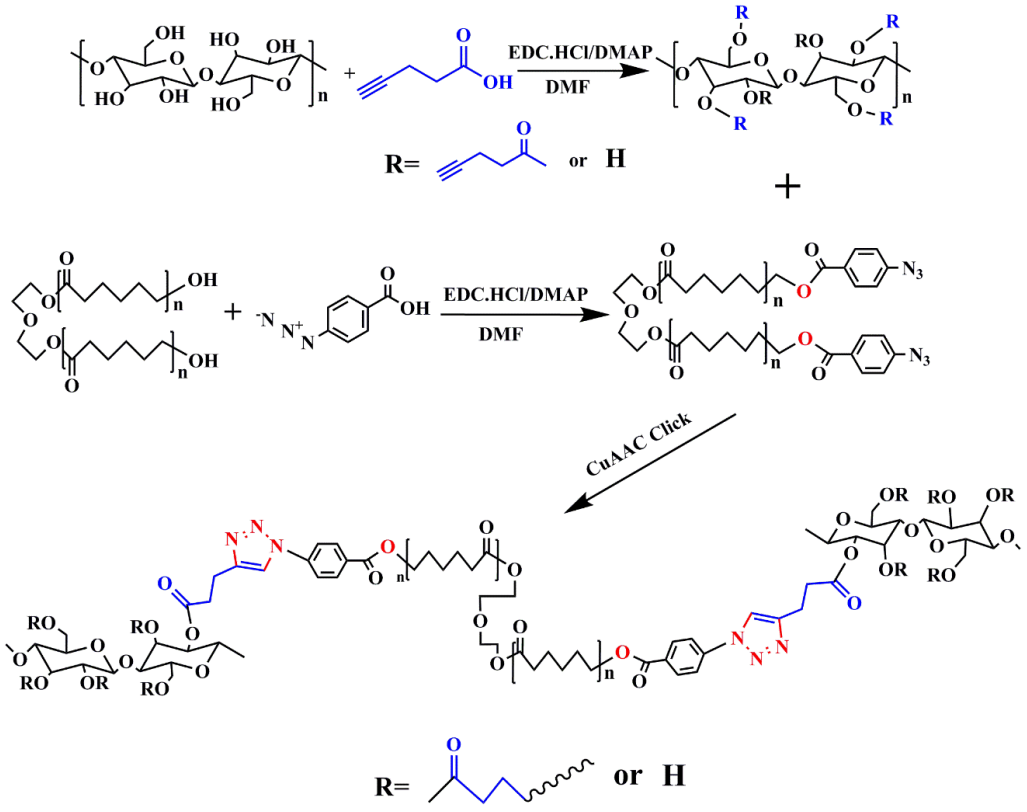

Figure S1. The chemical synthesis route of CNC-PCL aerogel

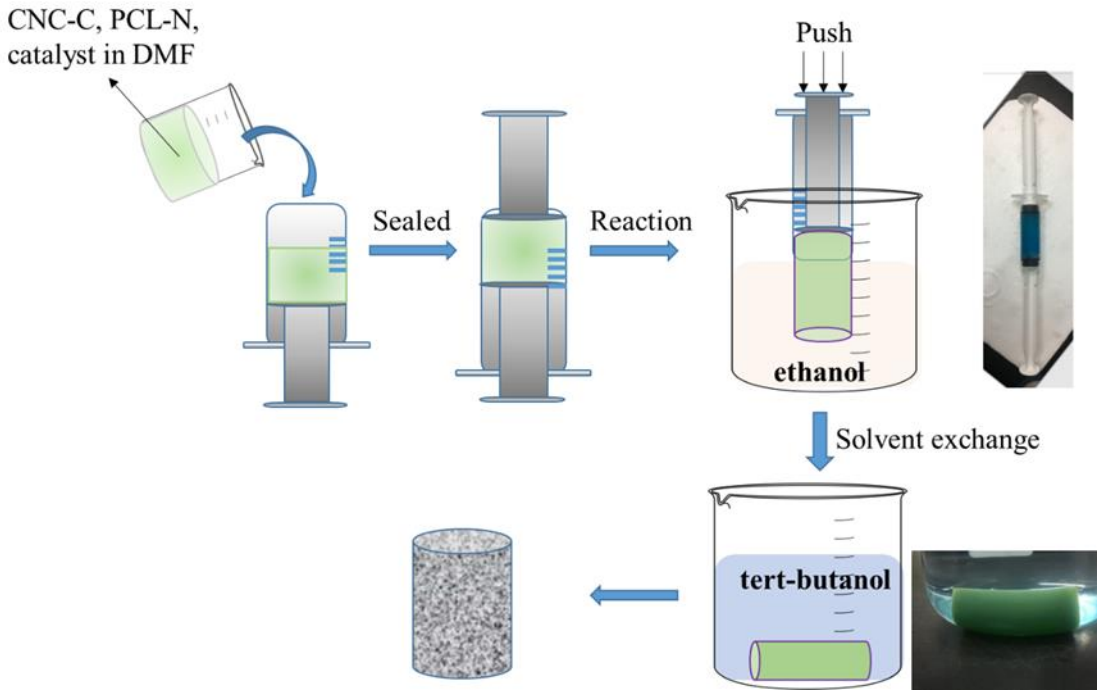

Figure S2. The preparation procedure of CNC-PCL aerogel

Equation for calculating the surficial hydroxyl groups

$$\boldsymbol{Rs = 2(\frac{d_{110}}{L1} + \frac{d_{1\bar{1}0}}{L2})}$$

Where Rs represents the ratio of the surficial hydroxyl groups, d110 and $d_{1\bar{1}0}$ represents the plane spacing of each of the crystal planes perpendicular to the faces of the crystal. For cellulose type Iβ, the planes $(1\bar{1}0)$ corresponding to 0.61 nm are parallel to the long side of the rectangular whisker section whereas the 0.54 nm (110) are parallel to the short side. L1 and L2 represent the height and width of the nanocrystal respectively[1].

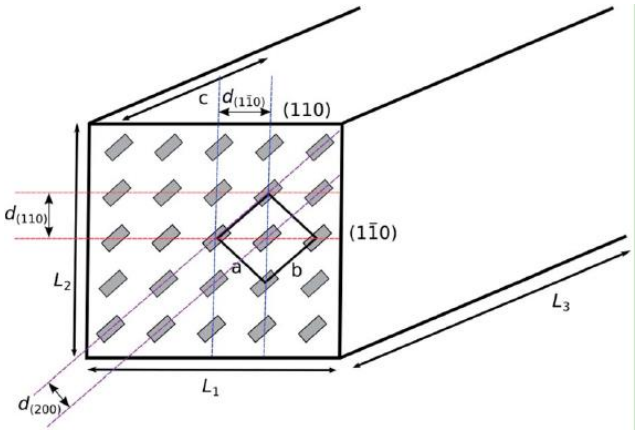

Figure S3. Model representation of a cellulose nanocrystal with cellulose chain ends in grey. The unit cell is depicted, along with the crystal planes exposed at the edges of the nanocrystal [1]

If we know the average diameter of CNCs (code as d) and consider L1and L2 both equal to d, the ratio of the surficial hydroxyl groups

$$\boldsymbol{Rs = 2\left(\frac{0.54}{d} + \frac{0.61}{d}\right) = \frac{2.3}{d}}$$

In addition, the fact that most reactions on cellulose nanocrystals have a reported DS<1.5 (completely surficial DS =3) of surface hydroxyl due to the crystal structure of CNCs where one C6, one C2 and one C3 hydroxyl point out of the face of the crystal for every two AGUs [2]. Therefore, the ratio of the reactive surficial hydroxyl groups can be calculated as blew

$$\boldsymbol{Rr = \frac{Rs}{2} = \frac{1.15}{d}}$$

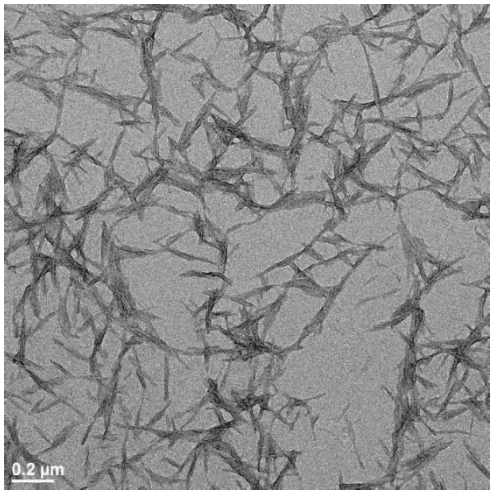

Figure S4. TEM image of the used CNCs providing by the manufacturer BLUE GOOSE BIOREFINERIES INC. Canada

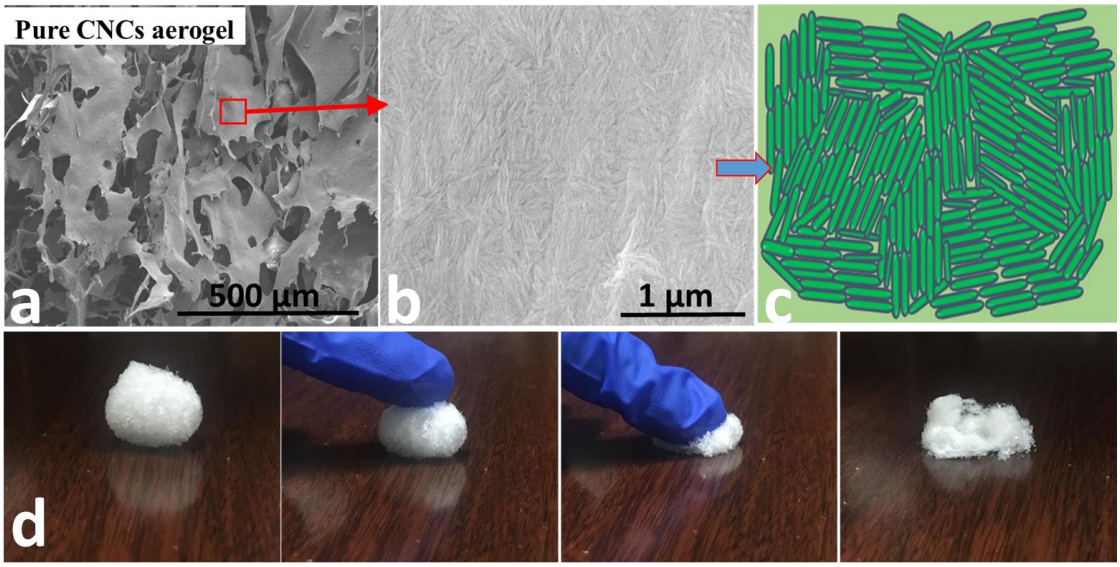

Figure S5. SEM images (a, b) of pure CNC aerogel obtained from freeze-drying from water and its construction scheme (c), and the digital images of its brittleness under compression

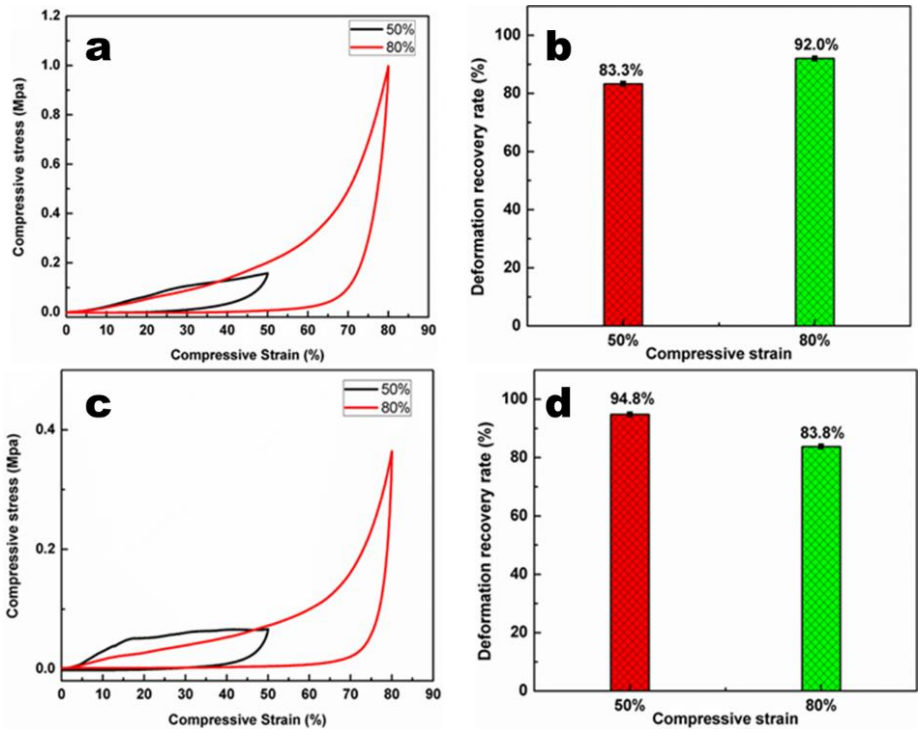

Figure S6. Typical tensile properties of CP-0.25-60 (a, b), and CP-0.25-140 (c, d) aerogels

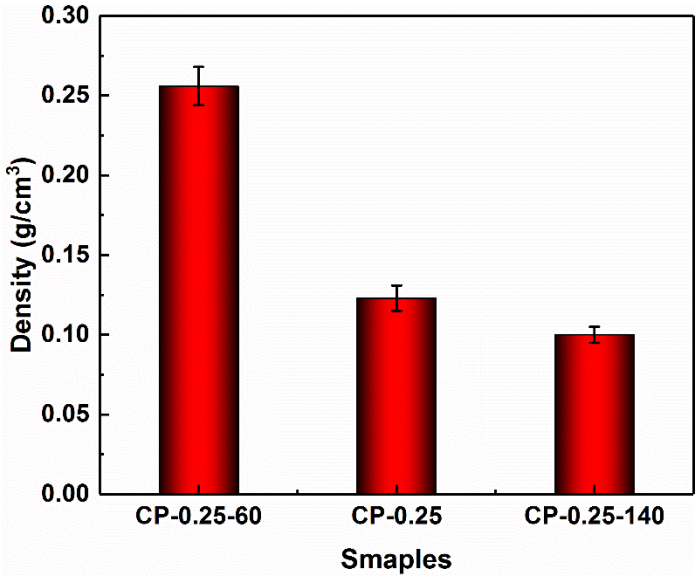

Figure S7. Density of CP-0.25 aerogels with various system concentrations

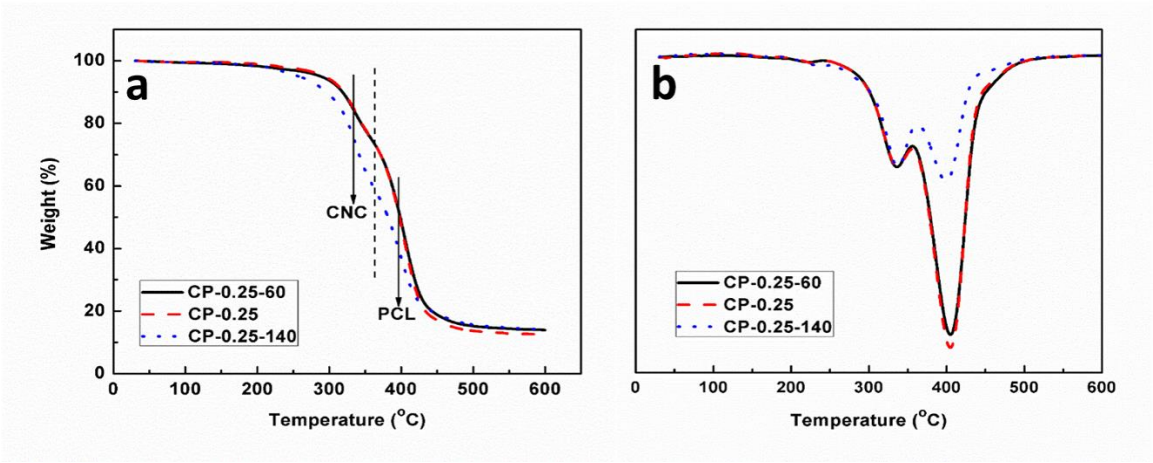

Figure S8. TGA (a) and DTG (b) of CNC-PCL aerogels with various system concentration

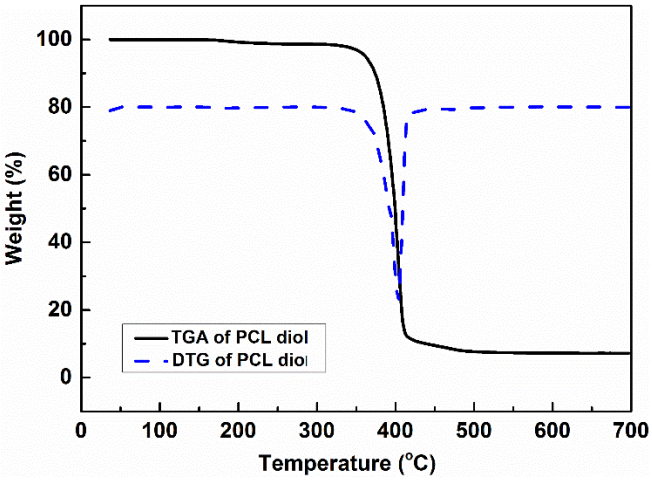

Figure S9. The TGA and DTG curves of PCL diol

Reference:

(1) Habibi, Y.; Chanzy, H.; Vignon, M. R. TEMPO-mediated surface oxidation of cellulose whiskers. *Cellulose* **2006,** *13* (6), 679-687.

(2) Eyley, S.; Thielemans, W. Surface modification of cellulose nanocrystals. *Nanoscale* **2014,** *6* (14), 7764-7779.