

## **Modulation of Assembly and Dynamics in Colloidal Hydrogels via Ionic Bridge from Cellulose Nanofibrils and Poly(ethylene glycol)**

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### **Extraction of Cellulose Nanofibrils by high-pressure homogenization**

The cellulose pulp suspension (5 wt%) was mechanically stirred for 24 h. Subsequently, the suspension was homogenized using an Ultra-Turrax (IKA) at 12,000 rpm for 1 h. This initially refining step was performed to increase accessibility of cell wall to the following mechanical shearing treatment. The pulp slurry (3 wt%) was pumping into a high-pressure fluidizer with two different Z-shaped chamber pairs. First, the slurry was passed into a chamber pair with a diameter of 400 and 200  $\mu\text{m}$  for 16 passes at 110 MPa, then 10 passed through a chamber pair with a diameter of 200 and 75  $\mu\text{m}$  for 12 passes at 170 MPa. The mixture was sonicated for 10 min (300 W) and converted to gel-like suspension with a solid content of 1.2 wt%.

### **TEMPO-Mediated Oxidation of Cellulose Nanofibrils**

Conversion of CNF to COOH-CNF, by oxidation of primary alcohol groups to carboxylic acid groups, was accomplished by the procedure reported in literature.<sup>1,2</sup> About 5 g of CNF was suspend in deionized water (400 mL) containing TEMPO (2,2,6,6-Tetramethylpiperidine-1-oxyl,  $\text{C}_9\text{H}_{18}\text{NO}$ ) 0.064 g, 0.4mM) and NaBr (0.4 g, 4 mM) and homogenized by ultrasonic treatment at an ice-water bath for 10 min. Then certain amount of NaClO aqueous solution (10 wt%, 5 mM per gram of cellulose) was slowly added to the suspension to start oxidization at room temperature with mechanical stirring (300 rpm). The pH of the system was maintained at 10 by adding 0.5 M NaOH throughout the reaction. The reaction was quenched by adding ethanol (10 mL), and 0.5 M HCl was slowly dropped into the mixture to adjust pH to 7. Finally, the oxidized CNF was throughout washed with water and then dialyzed to attain a water dispersion. The mass recovery ratio of the TEMPO-oxidized cellulose was  $\sim 75$  wt%.

The TEMPO-oxidized CNF has a carboxylated content of 1.45 mmol/g, which was determined by conductivity titration. The TEMPO-oxidized CNF was then suspend in water and homogenized by vigorous stirring for 30 min to a translucent cellulose nanofibril/water suspension. The diluted CNF was then centrifuged at 10,000 g for 15 min to remove the small amount of unfibrillated fraction or aggregates. The sediment was discarded and the supernatant was used for sample preparation.

Table S1 The studied compositions of CNF-PEG hydrogels by adding dispersed CNF suspension (5 mL) to an aqueous PEG solution (10 mL, 2 wt%).

Sample Code	CNF [5 mL] (g)	PEG [10 mL] (g)
CNF 0.2	0.01	0.2
CNF 0.4	0.02	0.2
CNF 0.5	0.025	0.2
CNF 0.8	0.04	0.2
CNF 1.5	0.075	0.2
CNF 2	0.1	0.2

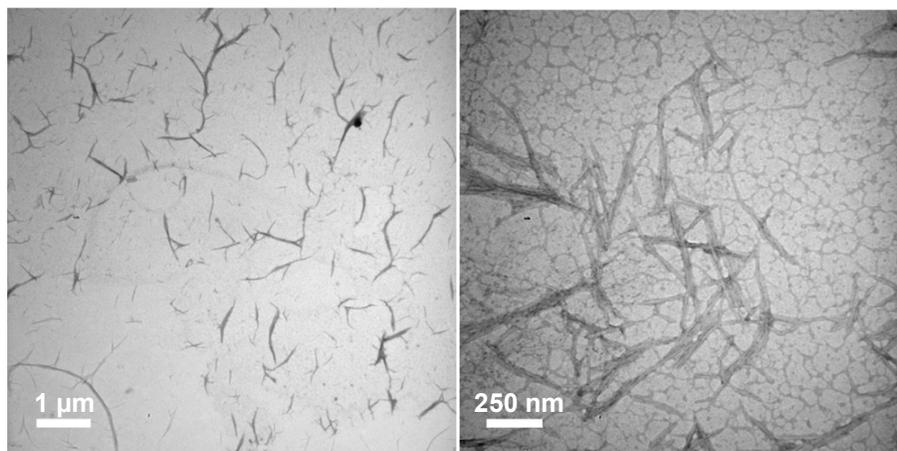


Figure S1. TEM image CNFs. To prepare the samples, 0.05wt% aqueous solution of CNF dispersions were drop-cast on carbon-coated copper grids and stained with 2 wt% uranyl acetate for 20 s.

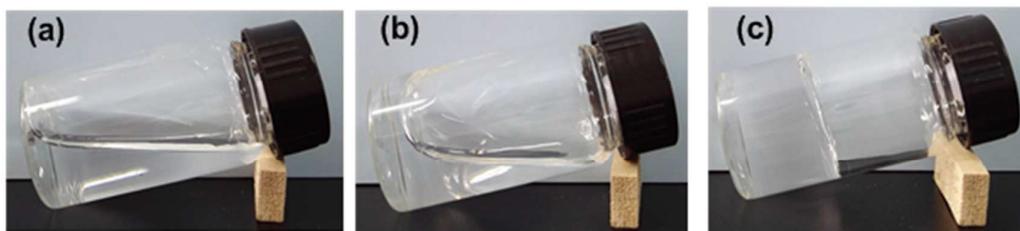


Figure S2. Photographs of CNF-PEG hybrids at different CNF loadings (a) 0.2 wt%, (b) 0.4 wt% and (c) 0.5 wt%, respectively.

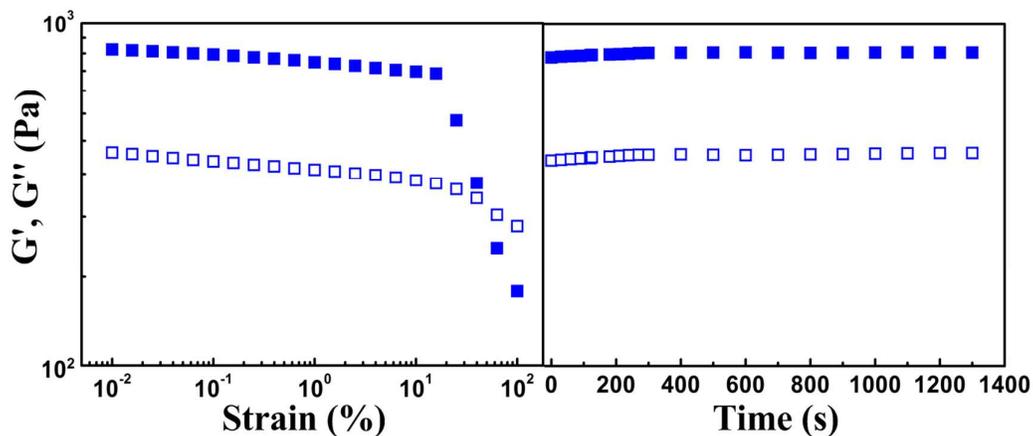


Figure S3. Strain sweep measurements of CNF 2 hydrogel at 25 °C for storage modulus (solid) and loss modulus (open) as a function of strain (left) and fast recovery from the 80% strain deformation (right). The  $G'$  and  $G''$  remained almost constant until the strain reached 25.1%, indicating the obtained hydrogel could withstand relatively large deformations. As the applied strain  $\gamma$  was further increased, a dramatic drop in both  $G'$  and  $G''$  was noted and a cross-over occurred at a strain of  $\gamma = 63\%$ , suggesting beyond this critical point dislocation of ionic bridges and damage of the cross-linked networks occurred and led to a sol state. It was noted that the mechanical properties of the hydrogel can be recovered if a 1% strain was immediately followed after large strain deformation ( $\gamma = 80\%$ ) within a short time ( $\approx 20$  s).

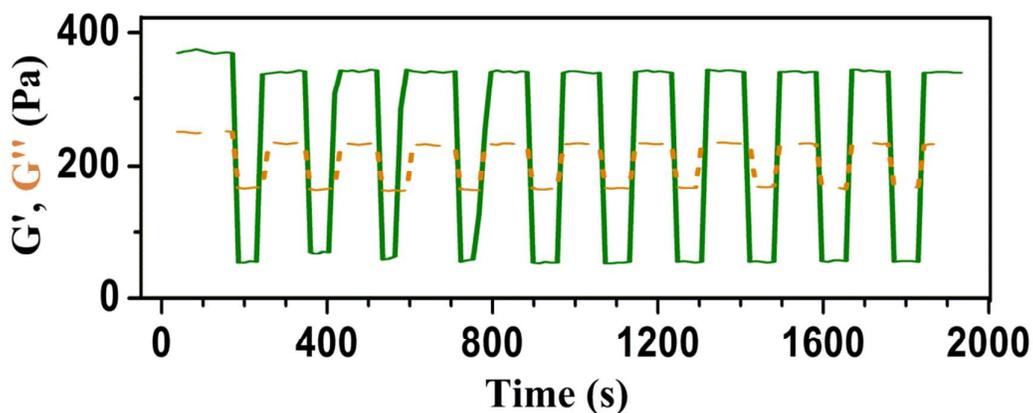


Figure S4. Dynamic strain amplitude cyclic test ( $\gamma = 1\%$  for 120 s and  $\gamma = 80\%$  for 60 s) of CNF 0.8 hydrogel at 25 °C.

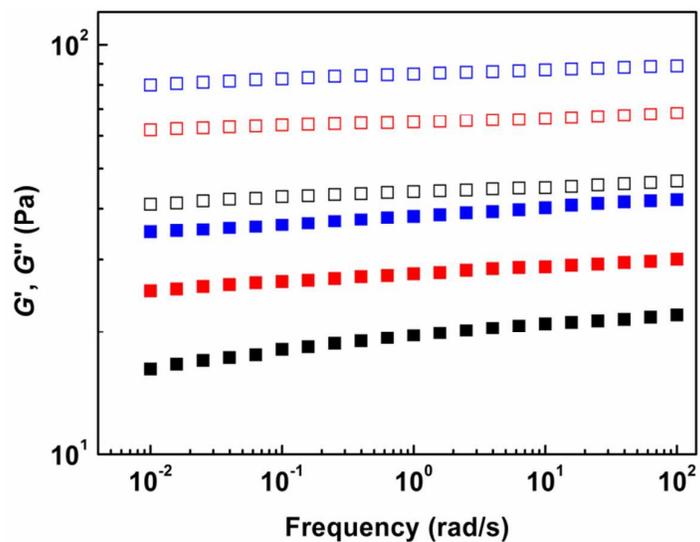


Figure S5.  $G'$  (solid) and  $G''$  (open) values of CNF aqueous suspension at concentration of 0.8% (black), CNF 1.5% (red), and CNF 2% (blue) on frequency sweep from 0.01 to 100 rad/s at room temperature.

#### References

- (1) Saito, T.; Kimura, S.; Nishiyama, Y.; Isogai, A. Cellulose Nanofibers Prepared by TEMPO-Mediated Oxidation of Native Cellulose. *Biomacromolecules* 2007, 8, 2485–2491.
- (2) Shinoda, R.; Saito, T.; Okita, Y.; Isogai, A. Relationship between Length and Degree of Polymerization of TEMPO-Oxidized Cellulose Nanofibrils. *Biomacromolecules* 2012, 13, 842–849.