# Electronic supplementary information

## Simple approach to reinforce hydrogels with cellulose nanocrystals

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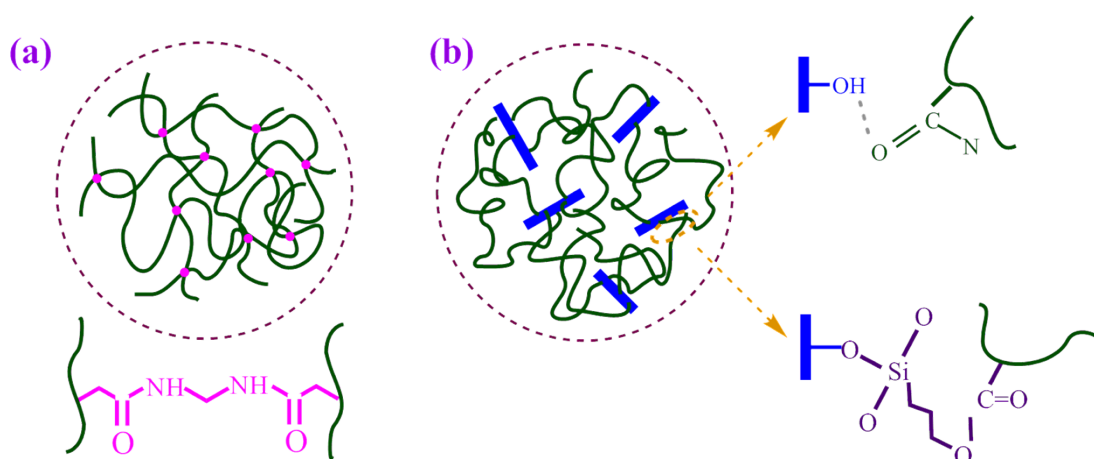
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Fig.S1 Scheme of (a) chemically cross-linked and (b) CNC loaded physically cross-linked networks.

**Conductomeric titration** Surface charges of CNCs that produced by sulfuric acid hydrolysis was determined by conductomeric titration. About 5 mL of CNC suspension (2 mg/mL) was poured into a 100 mL beaker with 60 mL sodium chloride aqueous solution (0.1 mM) under magnetic stirring during the whole titration. The sodium hydroxide solution (5 mM) was dropped into the suspension and the resistance was monitored using a resistance meter. The surface charges (termed as sulfur content, assuming that charges are present as $OSO_3^-$), $S$, were calculated by the volume of added NaOH according to following equation:[1]

$$s(\%) = \frac{32NV}{w_t W} \times 100 \qquad (1)$$

where $N$ and $V$ are concentration and volume of added NaOH solution, respectively, $w_t$ is the weight of poured suspension, and $W$ is the weight percentage of CNC suspension. The conductomertric titration results indicate that the surface charge concentration is 83 $OSO_3^- kg^{-1}$ for cellulose nanocrystals in this study.

**X-ray Photoelectron Spectroscopy** (XPS)

The silane modification through γ–methacryloxypropyl trimethoxy silane (A174) grafting on the surface of CNCs was analyzed by XPS. The experiments were conducted using PHI-5300 ESCA (Perkin Elmer) operated at 15 kV under a current of 10 mA. Samples were set in an ultrahigh vacuum chamber ($10^{-8}$ mbar) with electron collection by a hemispherical analyzer at a 90°angle. The silane agent grafting efficiency (GE%) was calculated as follows:

$$GE\% \times C_{A174} + (1\text{-}GE\%)C_{CNC} = C_{CNC\text{-}g\text{-}A174}$$

where $C$ is the relative silicon of the sample. There was new signal corresponding to silicon (288.5 eV) that assigned to the surface chemistry of CNC-g-A174 in comparison with pristine CNC, indicating covalent coupling from silylation reaction. The grafting efficiency (GE%) of silane agent was determined to be 6.8%.
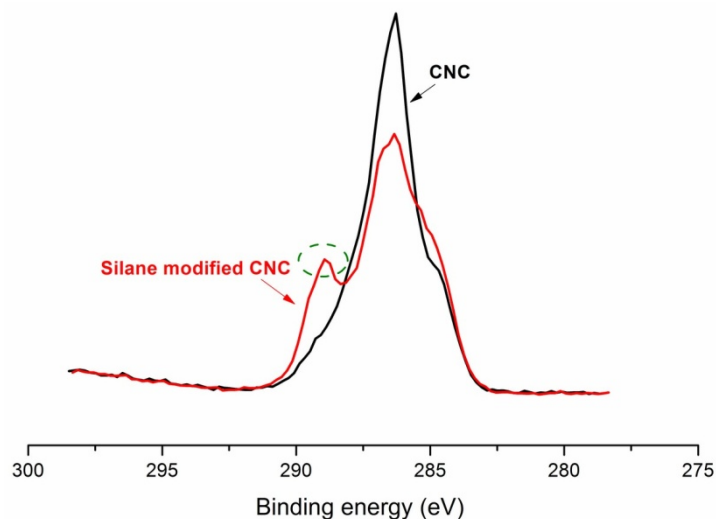


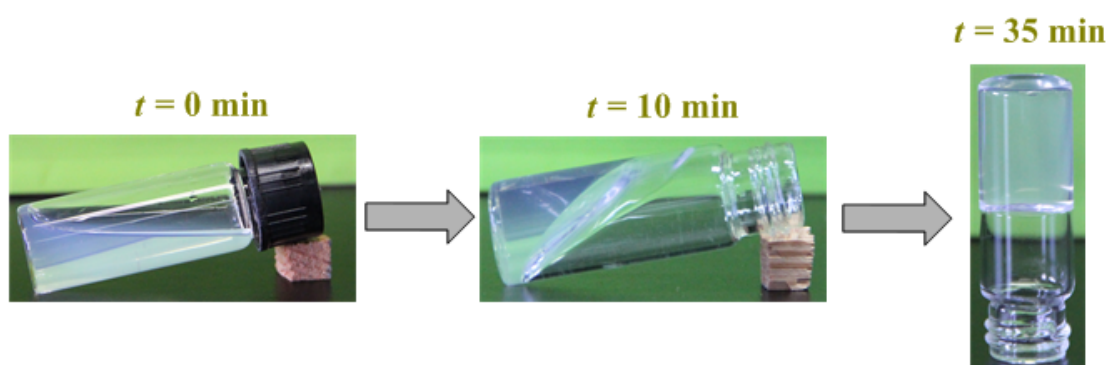Fig.S2 XPS spectra for CNC and silane modified CNC.



Fig.S3 Optical images of CNC20-PDMA15 gelation at different stages.

The macroscopic turbidity of CNC20-PDMA15 hydrogels should be the random distribution (hydrophilic cellulose and water-soluble monomer leading to good interfacial interactions) rather than aggregation process, due to the turbidity was already observed when the initially mixing CNC ($t$ = 0 min) and monomer and the turbidity did not significantly change during polymerization ($t$ = 10, 35 min).

The dried cubic samples ($1 \times 1 \times 1$ cm³) were weighted ($w_o$) and immersed into a large excess of water at room temperature. At time intervals, the cubes were taken out and dried at 65 °C with air-circulation oven for 48 h and weighted ($w_t$). The sample weight is calculated as follows: Sample weight% = $w_t/w_o \times 100\%$. Thus the extractable polymer fraction equals to (1- Sample weight%).
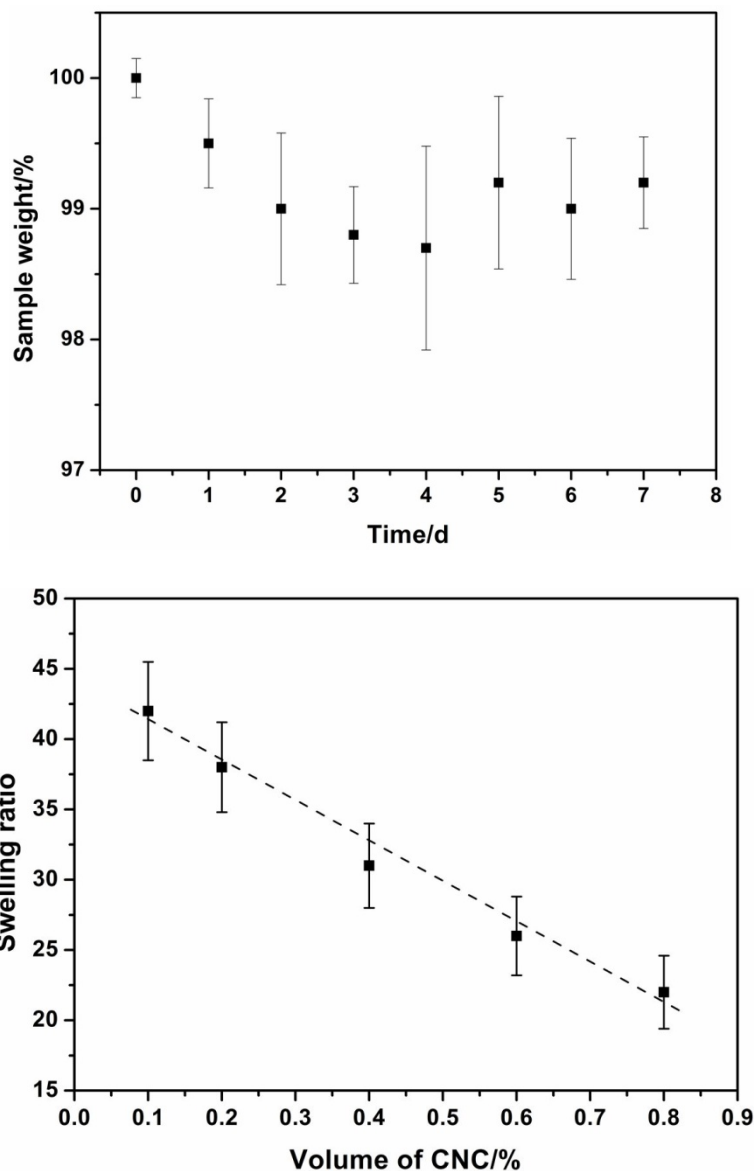
Fig.S4 (a) Weight loss of CNC40-PDMA15 gels as a function of swelling time at 25 °C, and (b) swelling ratio as a function of the volume fraction of CNC. There was almost no mass loss over 7 days, indicating integrity and stability of the network. Besides, the swelling ratio decreased with amount of CNC, suggesting the CNCs acted as multifunctional cross-links.

Heat induced dissolution

   To study the thermally induced gel-sol transitions, a swollen gel with water content of 1,000 wt% was prepared and gradually heated (heating rate 1 °C/min). According to the observation, the sample at 25 °C was free-standing gel, which kept immobile under its own weight when invert. Upon increasing the temperature to 55 °C, the sample began to flow under its own weight when tilted but remained mostly of bulk shape. With a further increase in temperature, it tuned into the free-flowing liquid with a low viscosity. In Fig.S5(a), the dissolution curves of associative gel were determined by the combination of glass-tube inverting method and mass loss ratio test (temperature range of 45-75 °C).
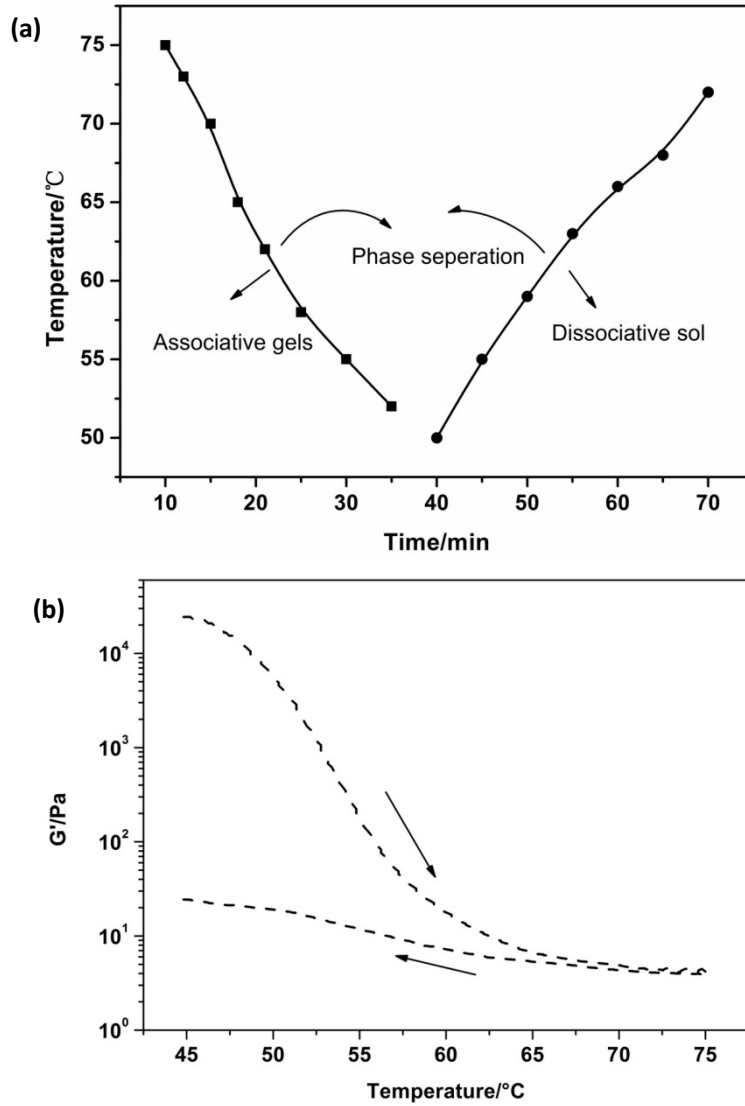
Fig.S5 (a) Dissolution curves and (b) thermo-irreversibility of storage modulus as a function of temperature for CNC20-PDMA15 gels at a frequency of 1 Hz. The arrows represent the heating and cooling curves.

To confirm the gel-sol reversibility, the measurement was conducted by heating the swollen hydrogels from 45 °C to 75 °C and then cooling to 45 °C again, and the evolution of storage modulus (G') as a function of temperature was recorded (Fig.S5(b)). One can note that the network shows almost an irreversible process and the modulus keep small, where it still appears solution state as the system cools down to the low temperature (45 °C).
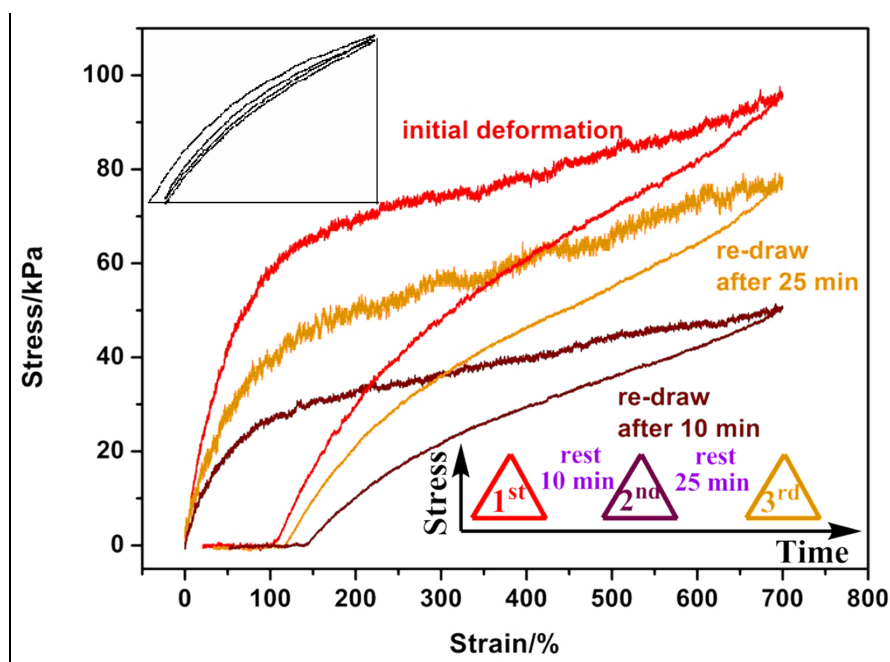
Fig.S6 Time-dependent of recovery in loading-unloading cycling behavior for CNC40-PDMA15 gels. The insert reveals a diagram of deformation-rest time experiments.

The successive loading-unloading cycle is a most useful indicator of internal self-healing capability, and the repeated cycles for CNC gels are showed in Fig.S6. One can note that as the rest-time increases, the residual strain decreased and the cycling behavior was similar to that of the initial deformation behavior. Thus, the CNCs, acting as transient multifunctional cross-links, are able to interact reversibly with the anchored polymer chains and the "sacrificial" interactions avoid irreversible damage. Whereas for CC counterparts (upper left insert), there has a negligible hysteresis loop, suggesting poor strain energy dissipation due to the permanent cross-links.

Cryo-SEM

Cryo-scanning electron microscopy (Cryo-SEM) is a powerful technique for obtaining in situ images of the 3D network structure of gels. This process was conducted on mechanically stretched hybrid hydrogels using a cryotransfer system (Oxford CT1500). The cryo-fractured samples were immersed into liquid nitrogen and then cut with a knife. The cut samples were coated with gold and observed with a DSM 960 Zeiss SEM at -140 °C. Fig.S7 shows hydrogels before mechanical deformation ($\varepsilon = 0$) and in the stretched state ($\varepsilon = 300\%, 500\%$). At the 'unstretched' structure, the CNCs homogeneously disperse in the matrix. Whereas for 'stretched' state, the CNCs bind neighboring matrix and act as bridge to reinforce the network.
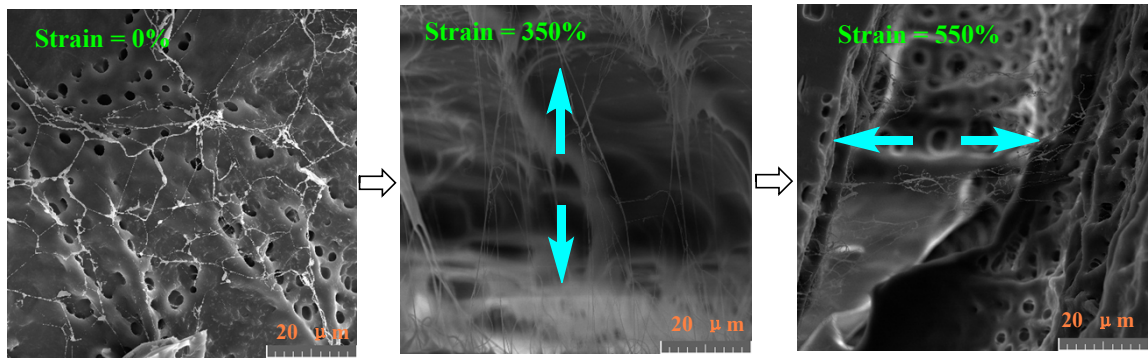
Fig.S7 Microstructure of CNC20-PDMA15 gel networks at different strains. The stretching direction is indicated by arrows.
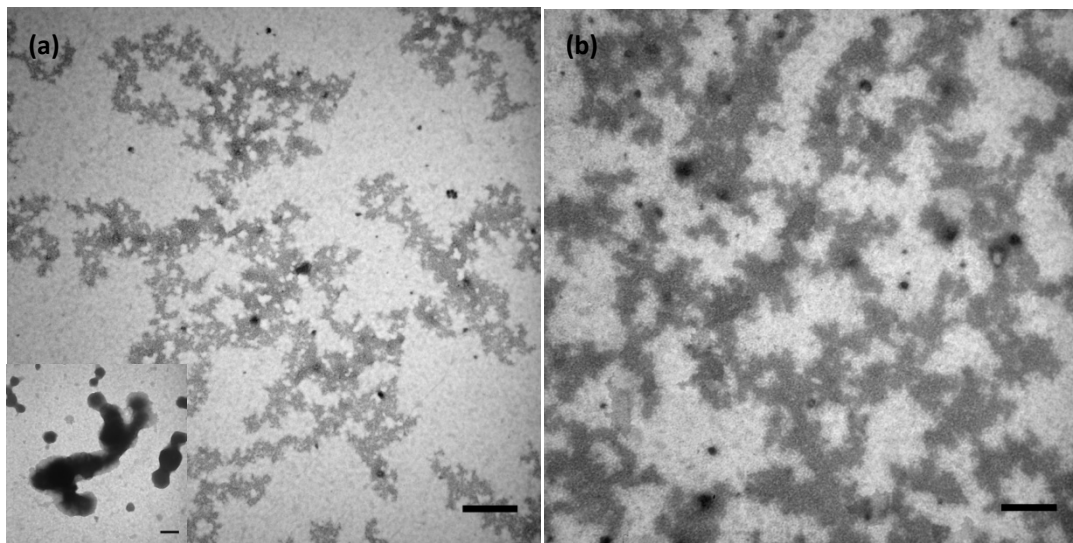


Fig.S8 TEM images of CNC-PDMA network with different PDMA contents. (a) It shows light gray at a PDMA content of 20 wt%, (b) whereas the polymer shell thickness increases and leads to small network pores at a polymer content of 40 wt% (bar = 100 nm). The local enlarged core-shell structure is demonstrated by the insert image in (a) (bar = 25 nm). The composition for samples (a) and (b) is list below:

| Sample | $m_{CNC}$ (mg) | $m_{DMA}$ (g) | $m_{BIS}$ (mg) | $m_{water}$ (mL) | $m_{Irgacure\ 2959}$ (mg) |
|---|---|---|---|---|---|
| (a) | 10 | 2 | - | 10 | 10 |
| (b) | 10 | 4 | - | 10 | 15 |

# References

1 X. M. Dong, J. F. Revol and D. G. Gray, *Cellulose* 1998, **5**, 19-32.