Facile fabrication of robust self-standing nanochitin hydro-/aerogel

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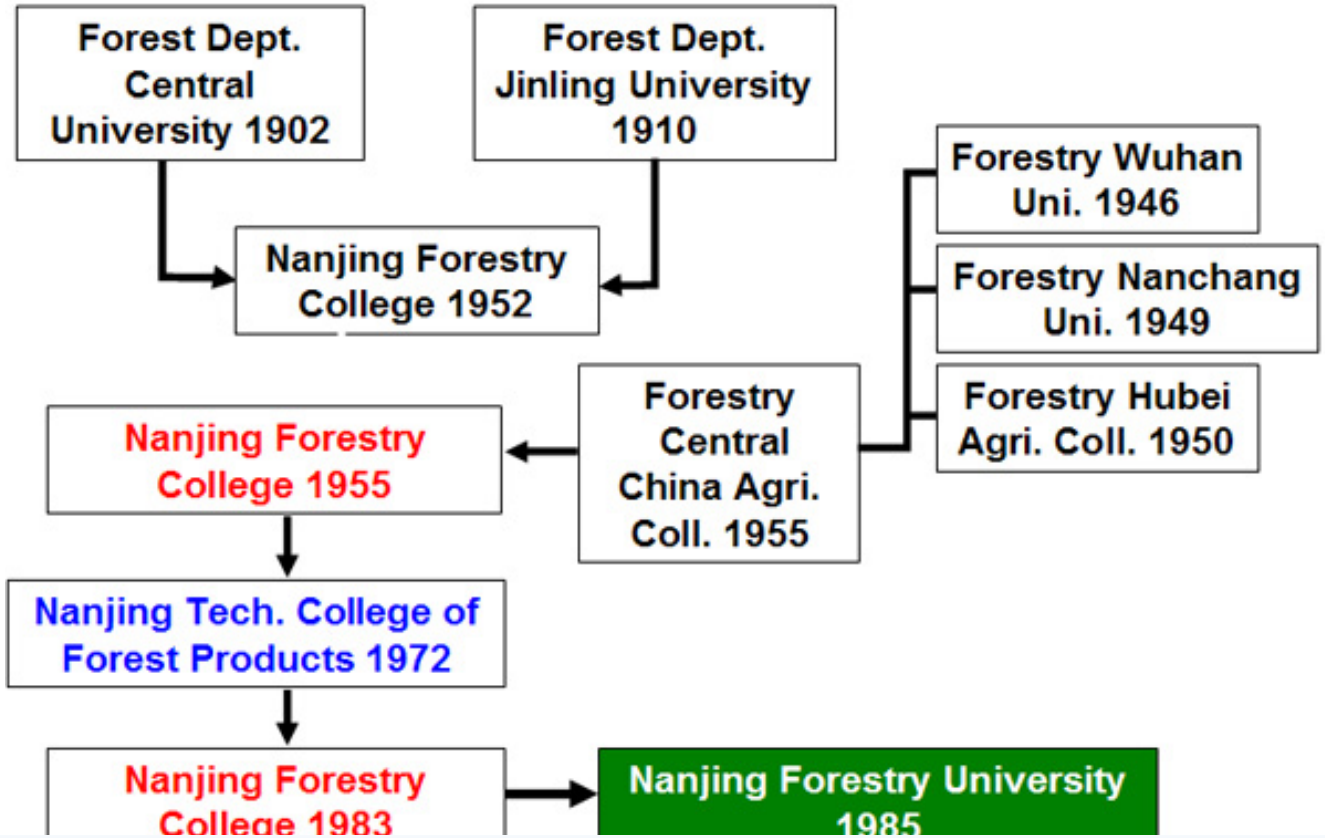
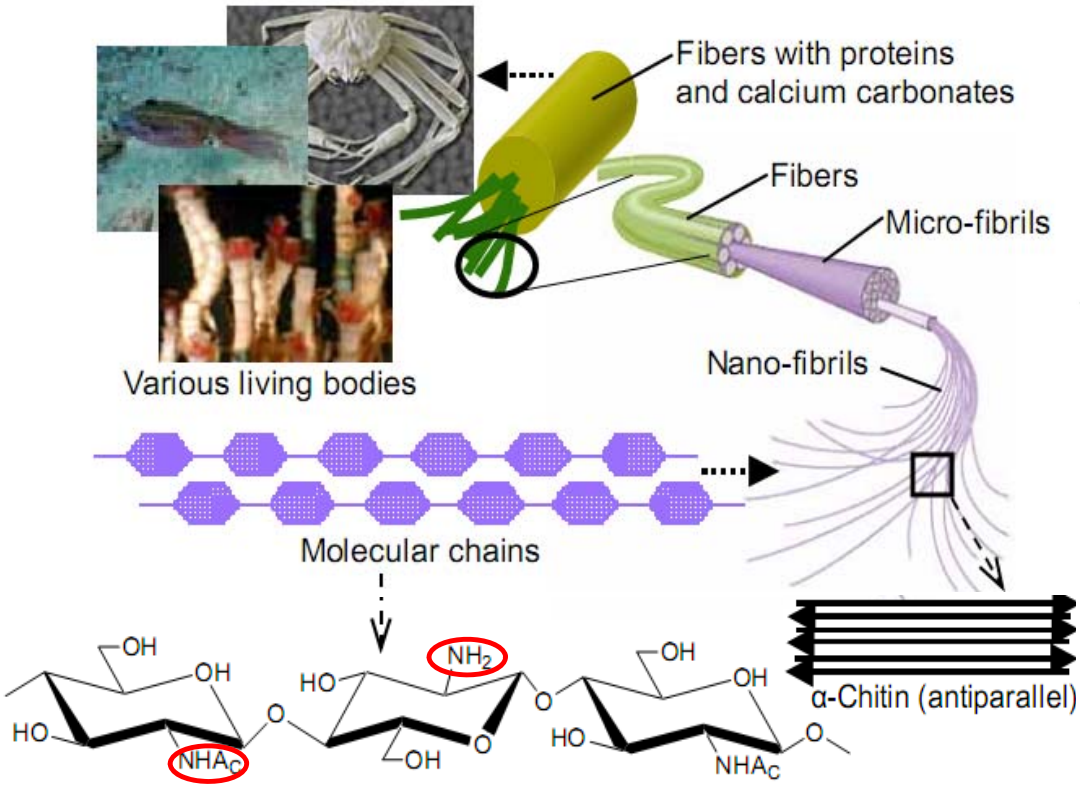
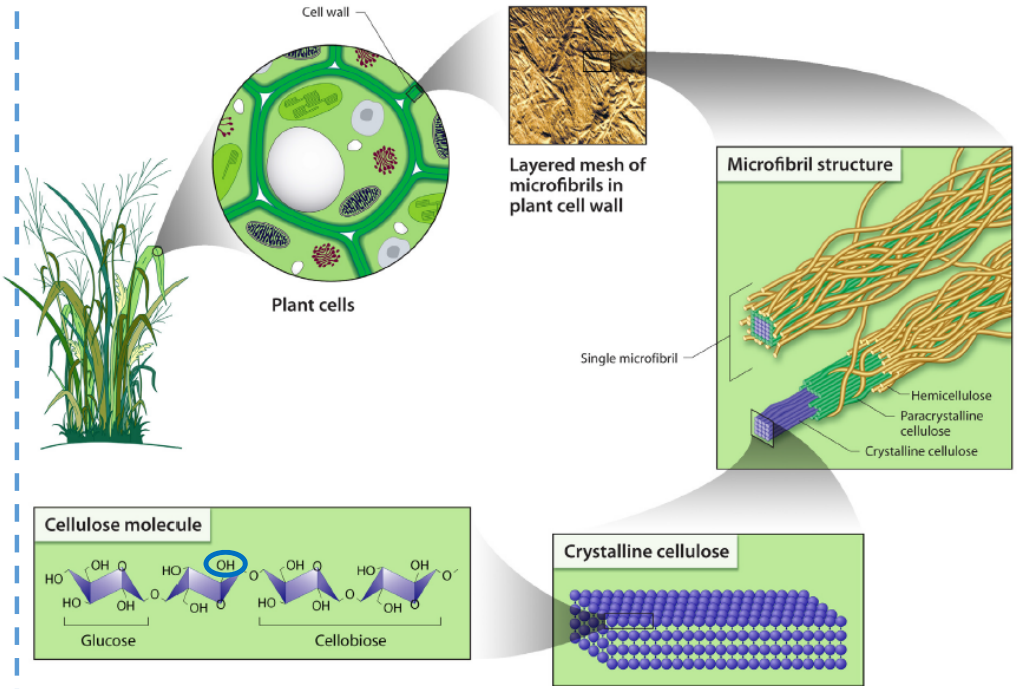
History of Nanjing Forestry University

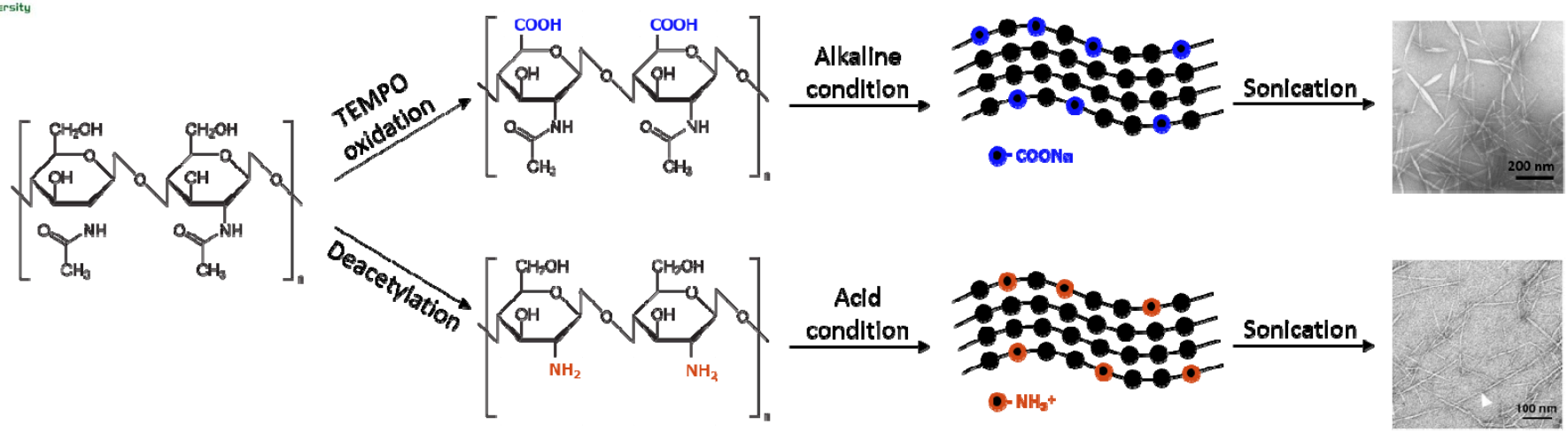


Chitin



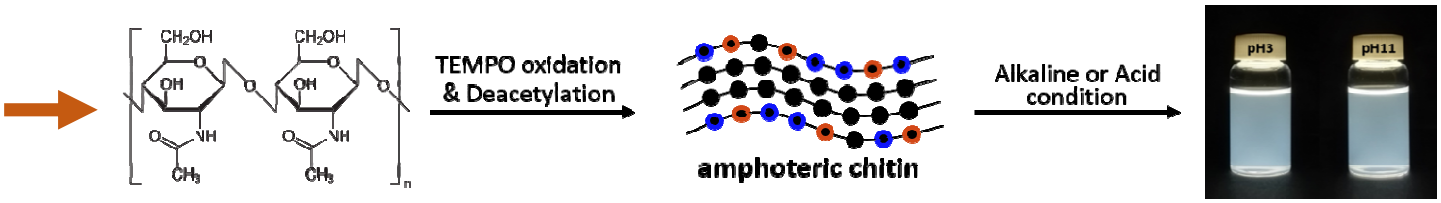
Cellulose





Fan Y, Saito T, Isogai A. Biomacromolecules, 2007, 9(1): 192-198.

Fan Y, Saito T, Isogai A. Carbohydrate polymers, 2010, 79(4): 1046-1051.



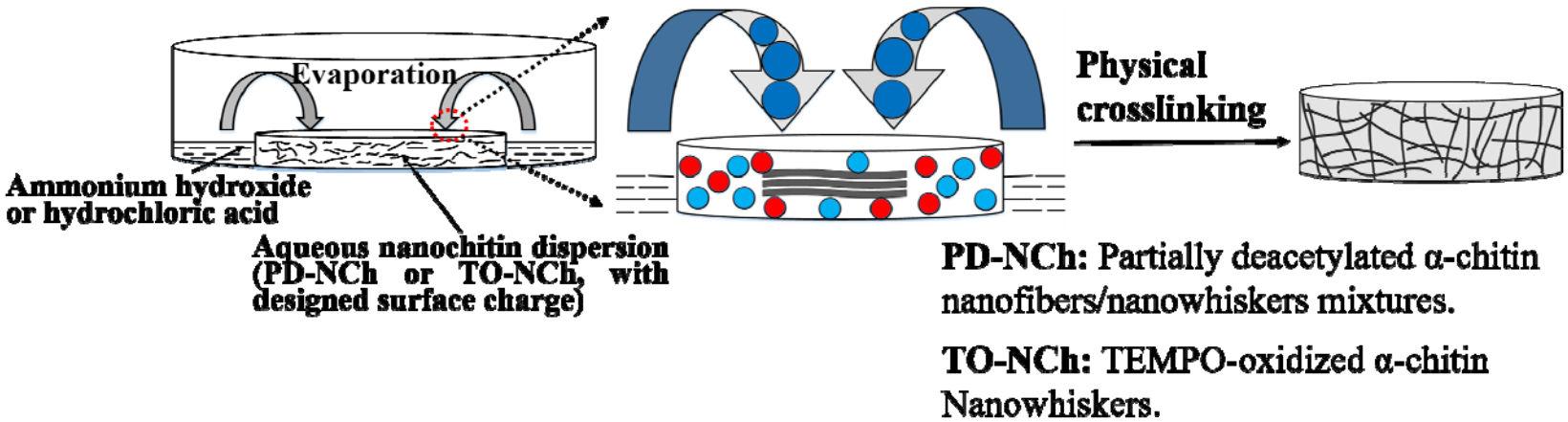
Jiang J, Fan Y, Saito T, Isogai A. Journal of Agricultural and Food Chemistry, 2018, 66(43): 11372-11379.

1. Gas phase induced physical crosslinking

2. Ice templated chemical crosslinking

3. Summary

Gas phase induced physical crosslinking



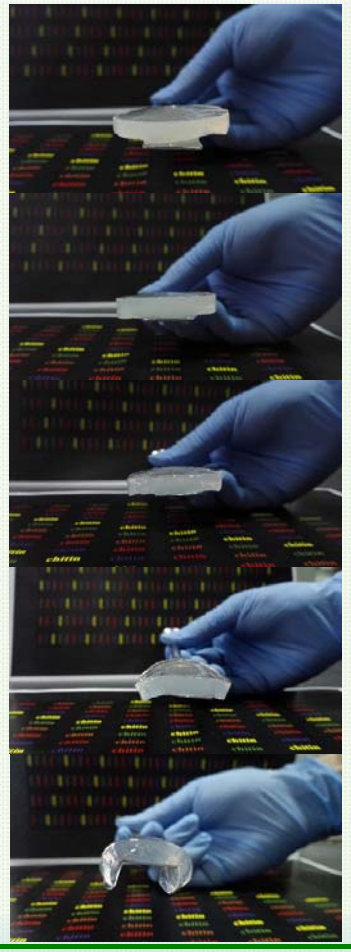
Formation scheme of physically crosslinked nanochitin hydrogels

- **Contact-free** and **mild gelation process** was key aspects for fabricating physical crosslinked nanochitin hydrogels.

Liu, L., Wang, R., Yu, J., Jiang, J., Zheng, K., Hu, L., ... & Fan, Y. (2016). Biomacromolecules, 17(11), 3773-3781.

Gas phase induced physical crosslinking

Decreased mass concentration



PD-NCh | TO-NCh

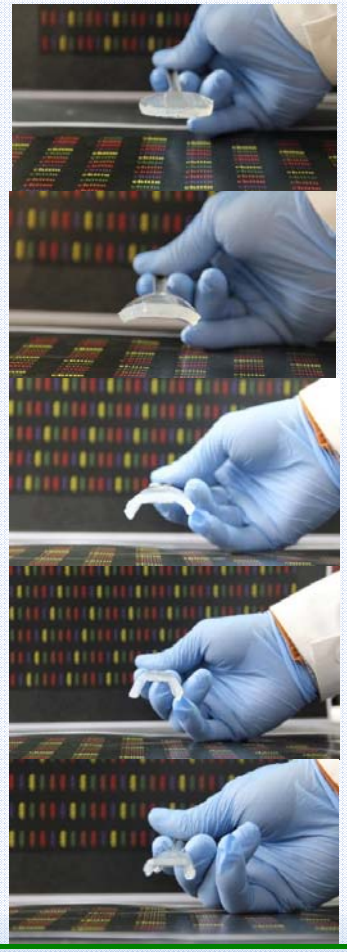
Mass content 1.0%

Mass content 0.8%

Mass content 0.6%

Mass content 0.4%

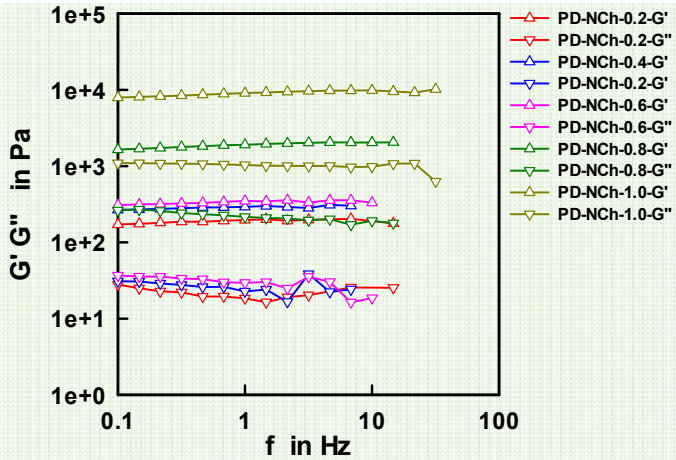
Mass content 0.2%

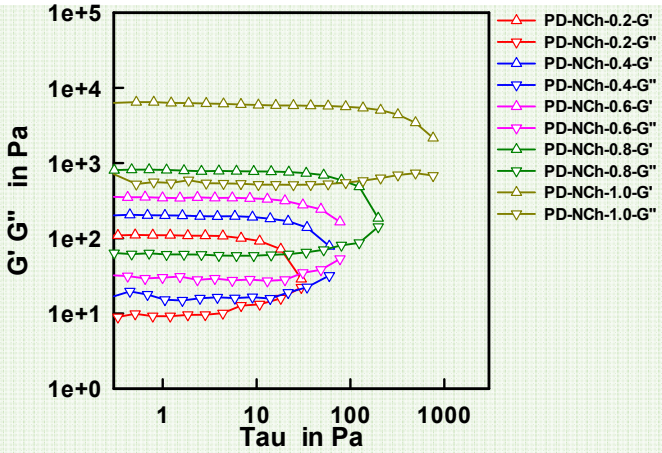


Increased mechanical strength

Gas phase induced physical crosslinking

PD-NCh

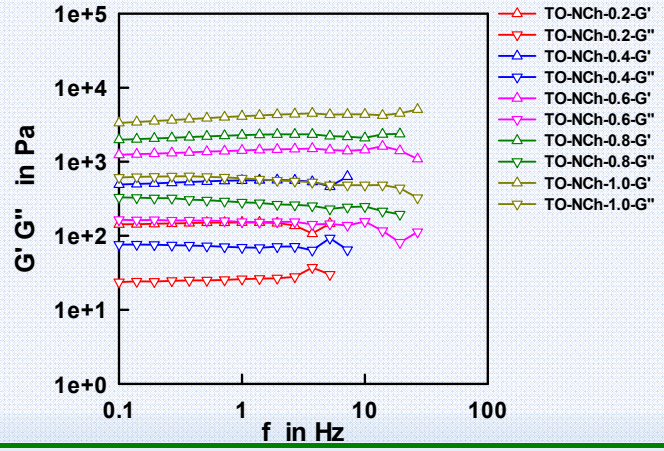


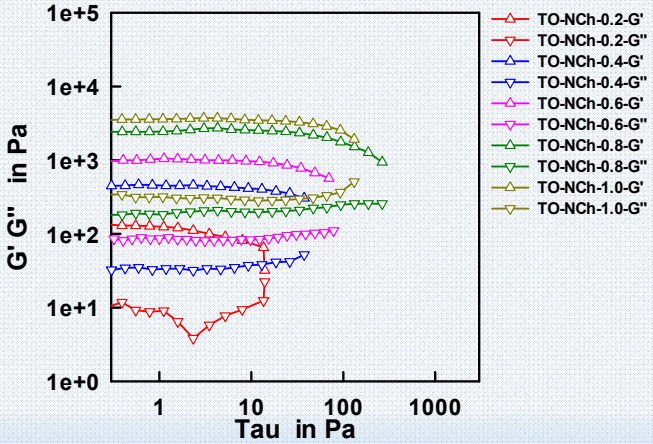


Frequency sweep

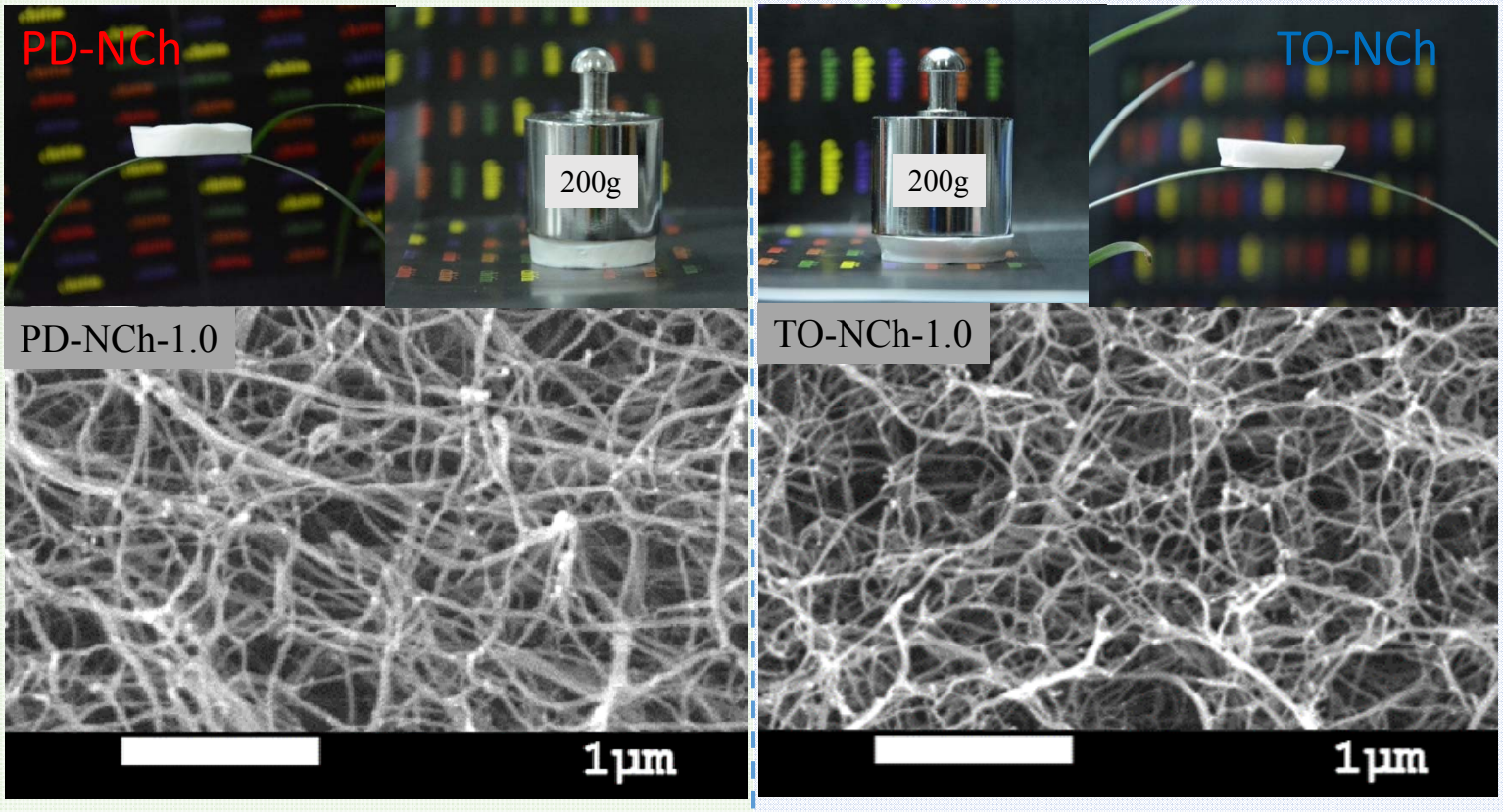
Stress sweep

TO-NCh





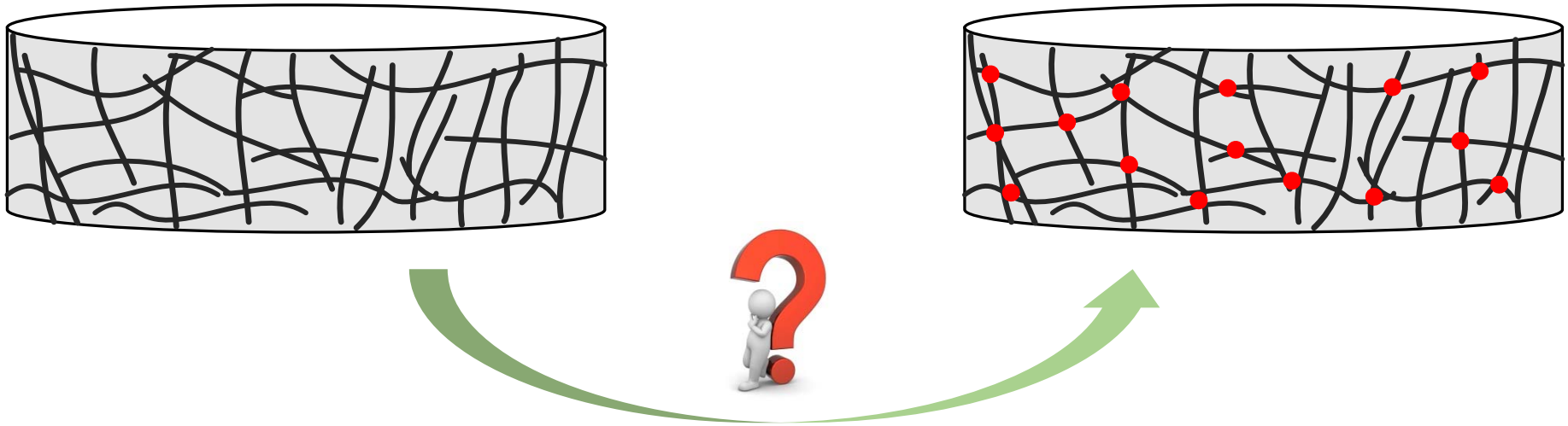
Gas phase induced physical crosslinking



➢NCh hydrogels/aerogels were supported by fiber-like textures which had diameters of approximately 10 nm.

Physical crosslinking

Chemical crosslinking



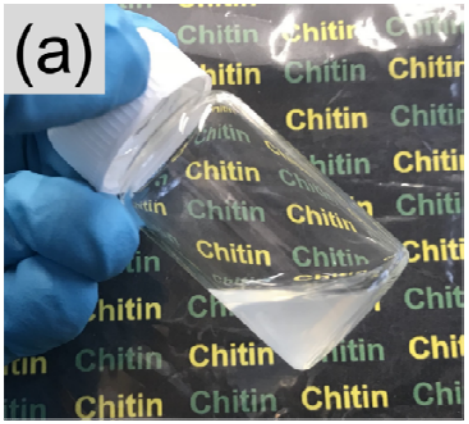
Better mechanical property

1. Gas phase induced physical crosslinking

2. Ice templated chemical crosslinking

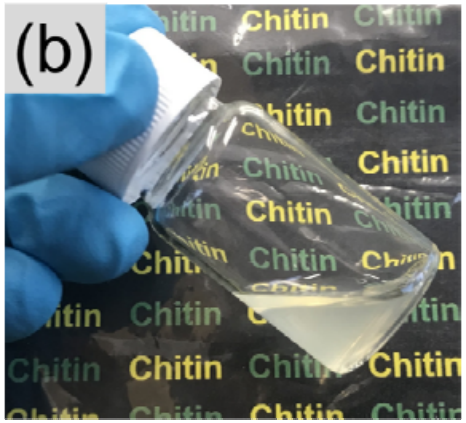
3. Summary

Ice templated chemical crosslinking

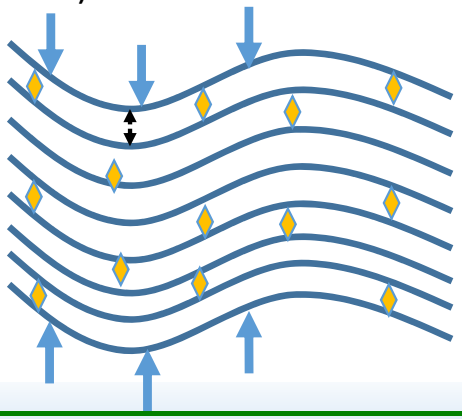


Freshly prepared nanochitin dispersion (0.4 wt%).

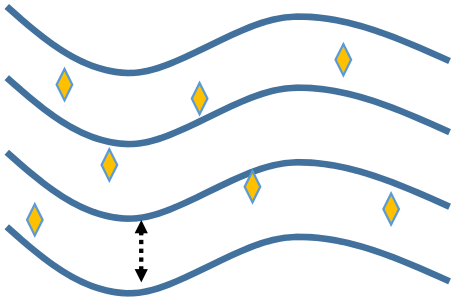
Well mixing with glutaraldehyde(Glu).



NCh(0.4)/Glu(0.4) dispersion keeping at room temperature for 7 days.

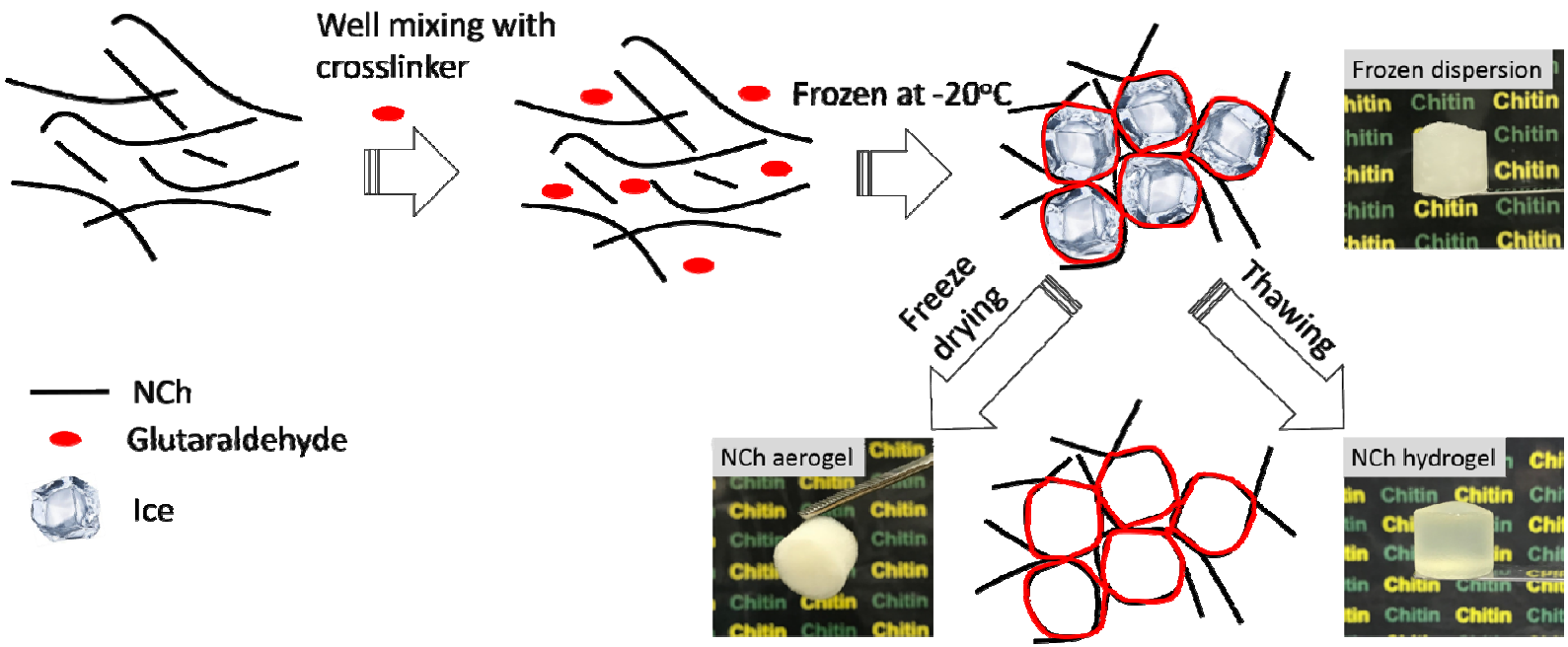


How to make nanochitins closer?



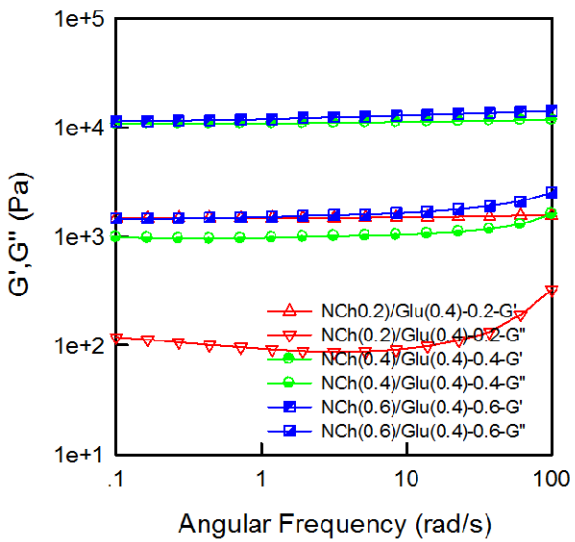
Unsuccessful crosslinking

Ice templated chemical crosslinking

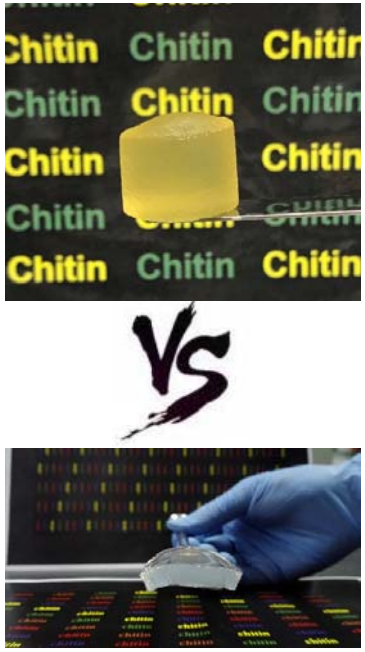


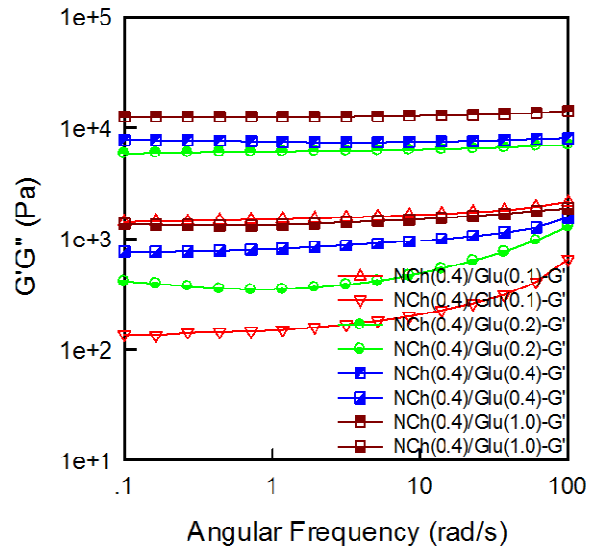
Formation scheme of chemically crosslinked nanochitin hydrogel/crycogel

Ice templated chemical crosslinking



Frequency sweeps of nanochitin hydrogel as a function of nanochitin concentration.

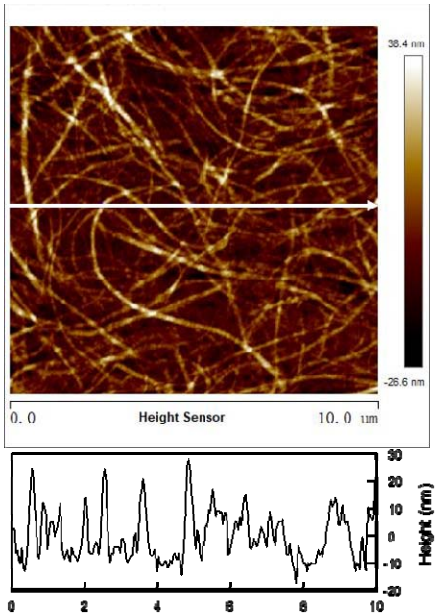




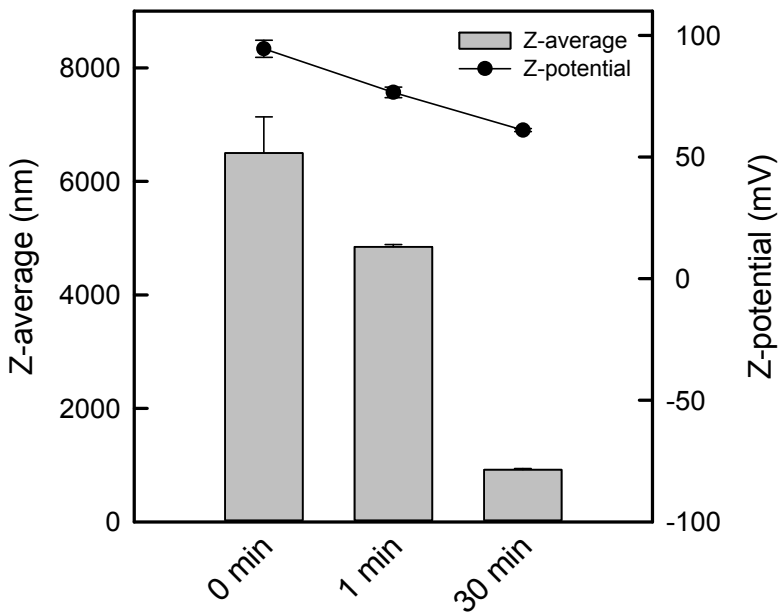
Frequency sweeps of nanochitin hydrogel as a function of glutaraldehyde dosage.

- Chemicaly crosslinked nanochitin hydrogel exhibited 52 times higher storage modulus comparing physically crosslinked nanochitin hydrogel (under mass concentration of 0.4%).

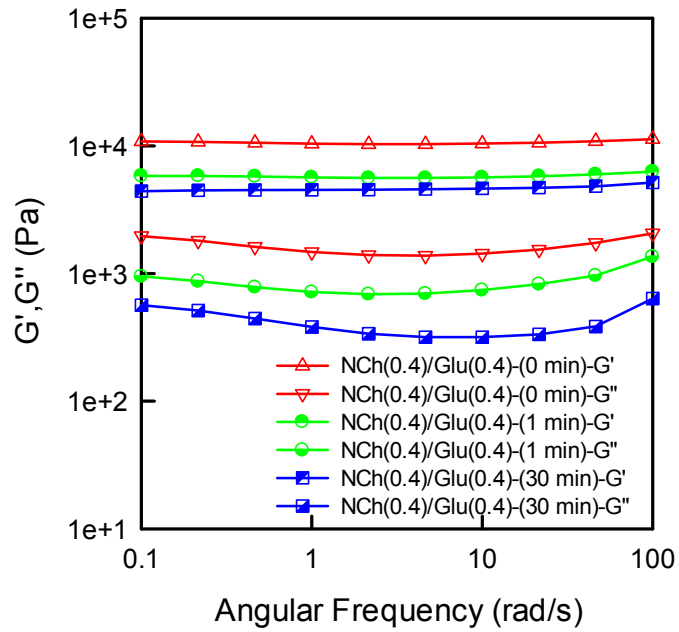
Ice templated chemical crosslinking



Aatomic force microscopy images of freshly prepared nanochitins (NCh).



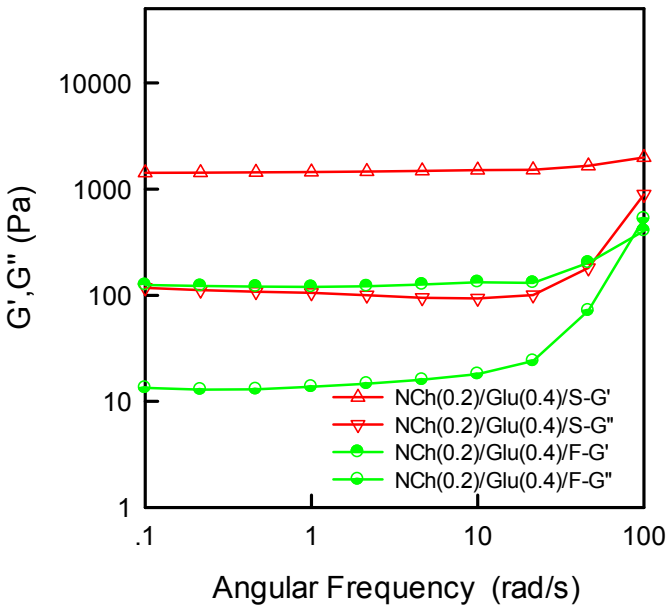
NCh fibril length (Z-average in nm, left axis) and ζ-potential (in mV, right axis) in aqueous suspension (indicative of colloidal stability) upon treatment with tip sonication for 0, 1, and 30 min.



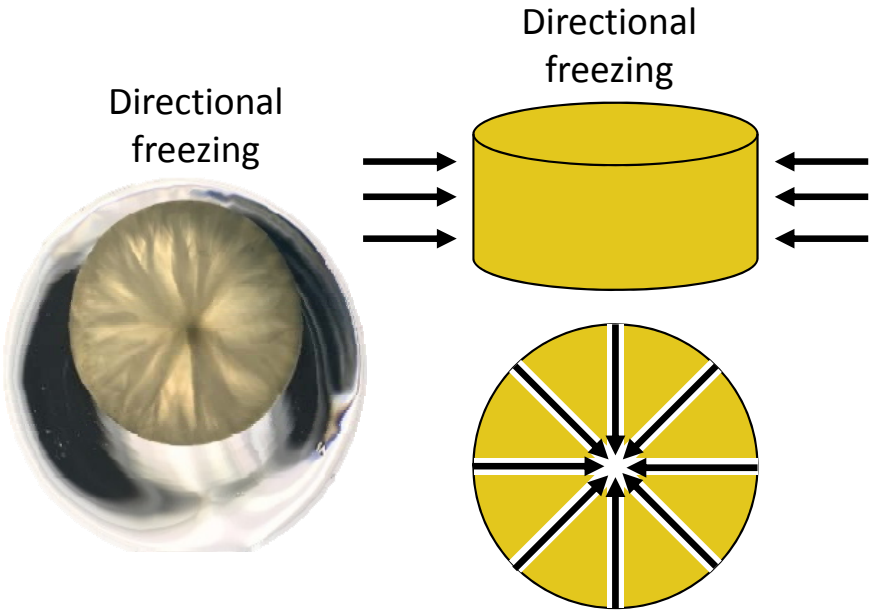
Frequency sweeps of nanochitin hydrogel as a function of fibril length in NCh(0.4)/Glu(0.4) hydrogels.

- As NCh fibril length increased, mechanical property of prepared nanochitin hydrogel also promoted.

Ice templated chemical crosslinking

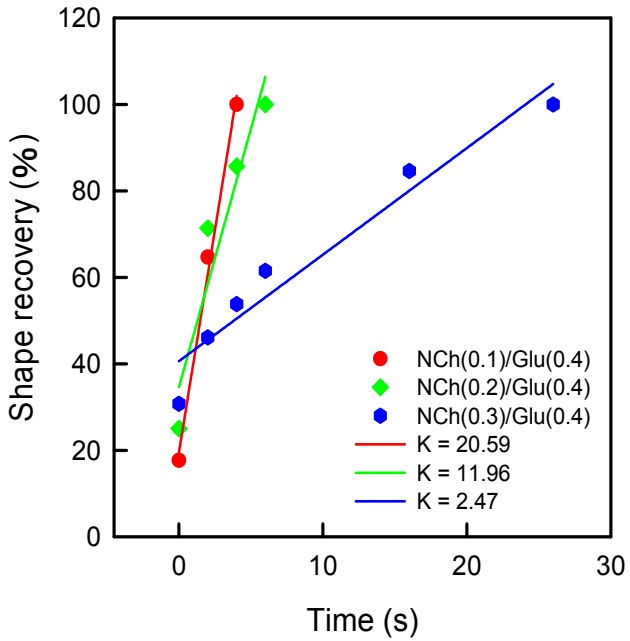


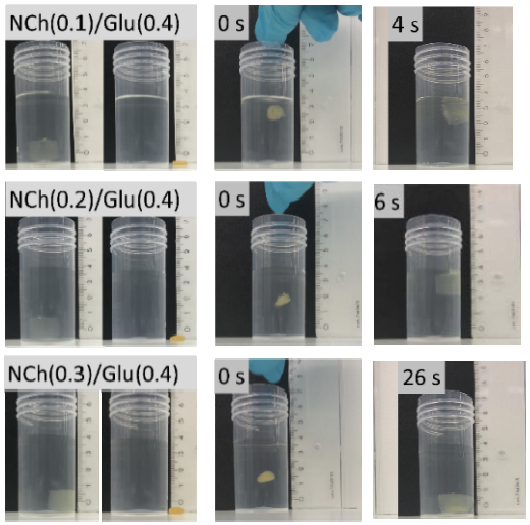
Frequency sweeps of nanochitin hydrogel as a function of freezing: (c) slow S (−20 ° C) and fast F (−196 ° C) freezing of NCh(0.2)/Glu(0.4) hydrogels.



Photographs of directional freezing in nanochitin hydrogels.

Ice templated chemical crosslinking

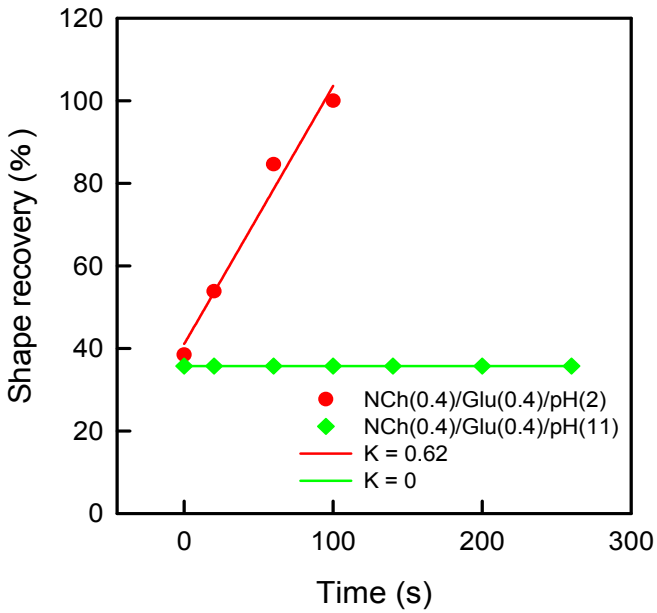


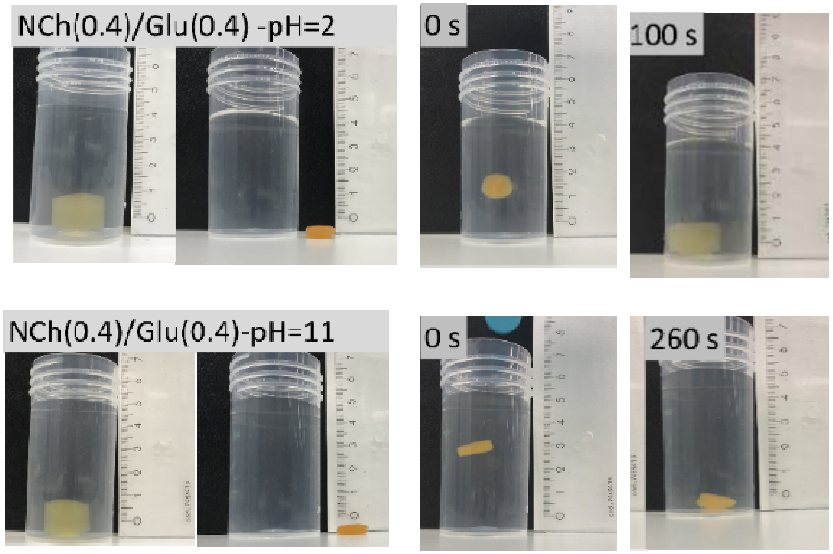


Dynamics of shape recovery, as indicated by the % recovery from the original height of NCh hydrogels immersed in water during the given time and as a function of the composition.

- Increased mass concentration of nanochitin hydrogel leaded to slower shape recovery property.

Ice templated chemical crosslinking



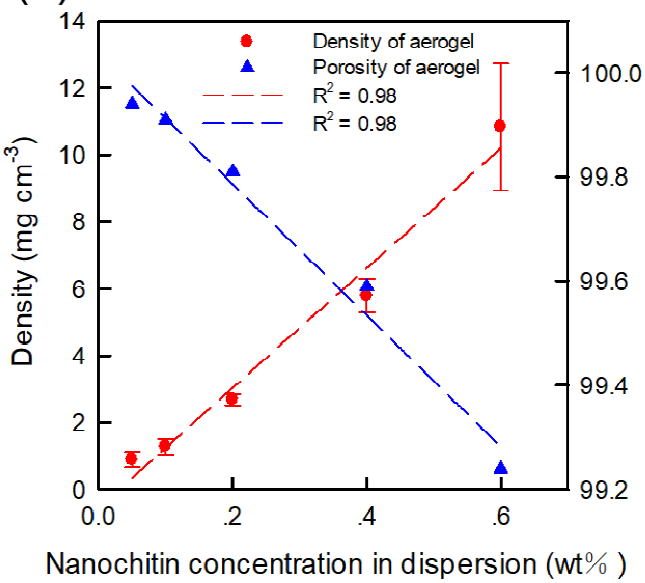


Dynamics of shape recovery for the NCh(0.4)/Glu(0.4) hydrogel after immersion in buffer solution at pH 2 and 11.

- Amino groups in partially deacetylated nanochitin resulted in pH dependent shape recovery property(sensitive in acid nature).

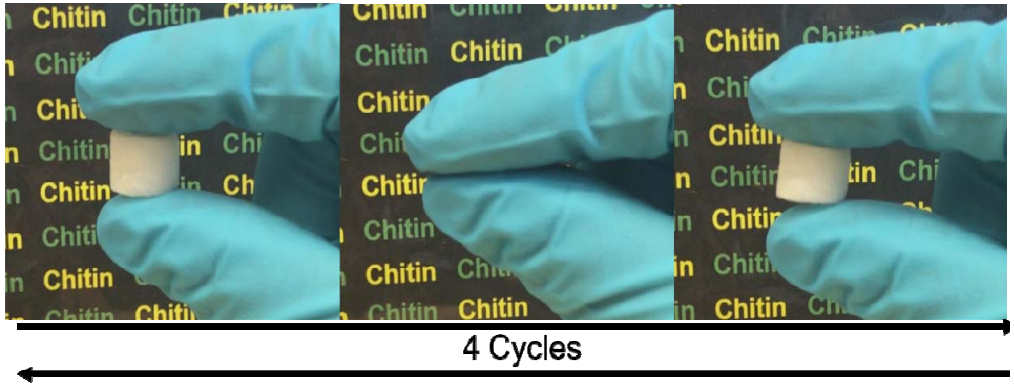
Ice templated chemical crosslinking

(a)



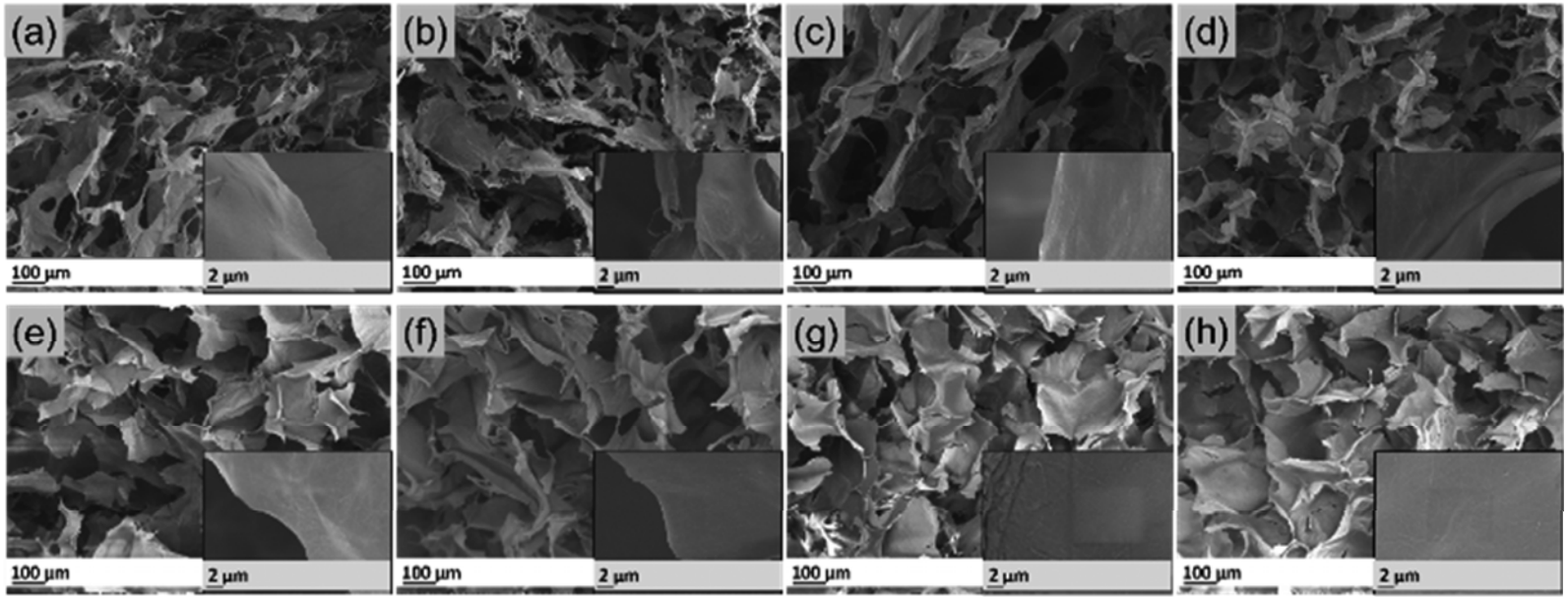
Density and porosity of nanochitin cryogels as a function of nanochitin concentration in the precursor suspension with 0.4 Glu/NCh mass ratio.

Photographs of NCh(0.1)/Glu(0.4) cryogel that was lifted with a plastic spoon by static electricity. The density and porosity of this cryogel was 1.53 mg·cm^{-3} and 99.89%, respectively.



- After freeze drying, prepared nanochitin cryogel was found ultralight and shape recoverable in the air.

Ice templated chemical crosslinking



SEM images of nanochitin cryogel prepared from different hydrogel compositions: (a) NCh(0.05)/Glu(0.4), (b) NCh(0.1)/Glu(0), (c) NCh(0.1)/Glu(0.4), (d) NCh(0.2)/Glu(0.4), (e) NCh(0.4)/Glu(0.1), (f) NCh(0.4)/Glu(0.4), (g) NCh(0.4)/Glu(1.0), and (h) NCh(0.6)/Glu(0.4). The insets correspond to images at higher magnification, highlighting the pore walls.

- Film-like pore walls were supported by assembled nanochitin fibrils and resulted the better mechanical property of chemical crosslinked nanochitin hydrogel/cryogel.

1. Gas phase coagulation bath

2. Ice templated chemical crosslinking

3. Summary

- Partially deacetylated nanochitin and TEMPO-oxidized nanochitin that had positive and negative charges, respectively, could be transformed into hydrogels under “gas phase coagulation”.

- Viscoelastic and strong nanochitin hydrogels could be formed by ice templating upon freezing and thawing with simultaneous cross-linking.

- Lyophilization was effective in producing cryogels with a density that could be tailored in a wide range of values, from 0.89 to 10.83 mg·cm−3, and corresponding porosity, between 99.24 and 99.94%.

- A fast shape recovery was registered from compressive stress−strain hysteresis loops. After over 80% compressive strain, the cryogels recovered fast and completely upon load release. The extreme values in these and other physical properties had not been achieved before for neither nanochitin nor nanocellulosic cryogels.

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Ten years in NFU

Aalto University

One year in Aalto

Thank you

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