Understanding the colloidal stabilization effect of nanochitin suspended with carbon nanomaterials towards energy materials

Tianyu Guo, Jing Tian, Gabriel Banvillet, Yi Lu, Zhangmin Wan, Yimin Mao, Orlando Rojas

PRESENTED BY:
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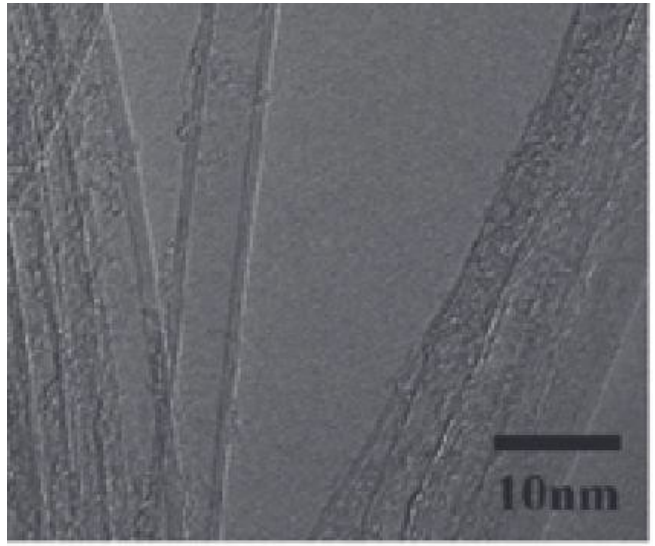
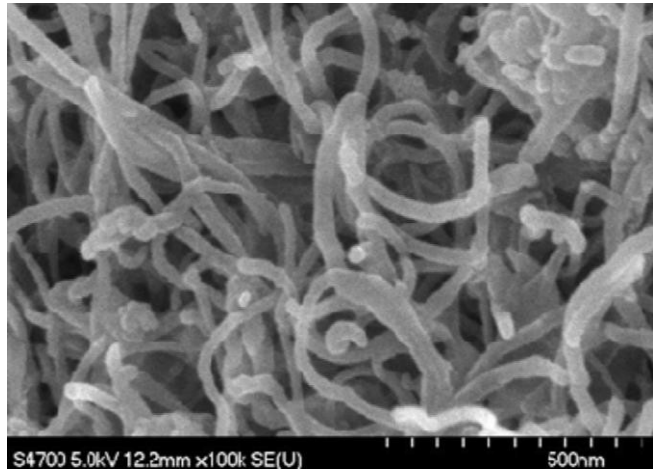
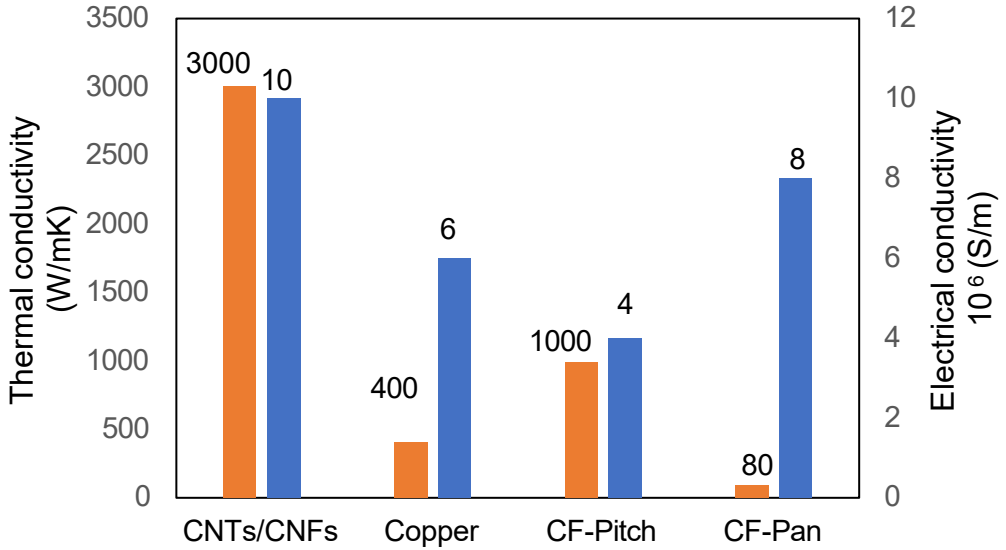
University of British Columbia

Carbon nanotube: Unique characteristics





Aspect ratio	Purity (%)	Surface area (m^2/g)	Bulk density (g/cm^3)
250-4000	95-99.8	100-650	0.05-0.25

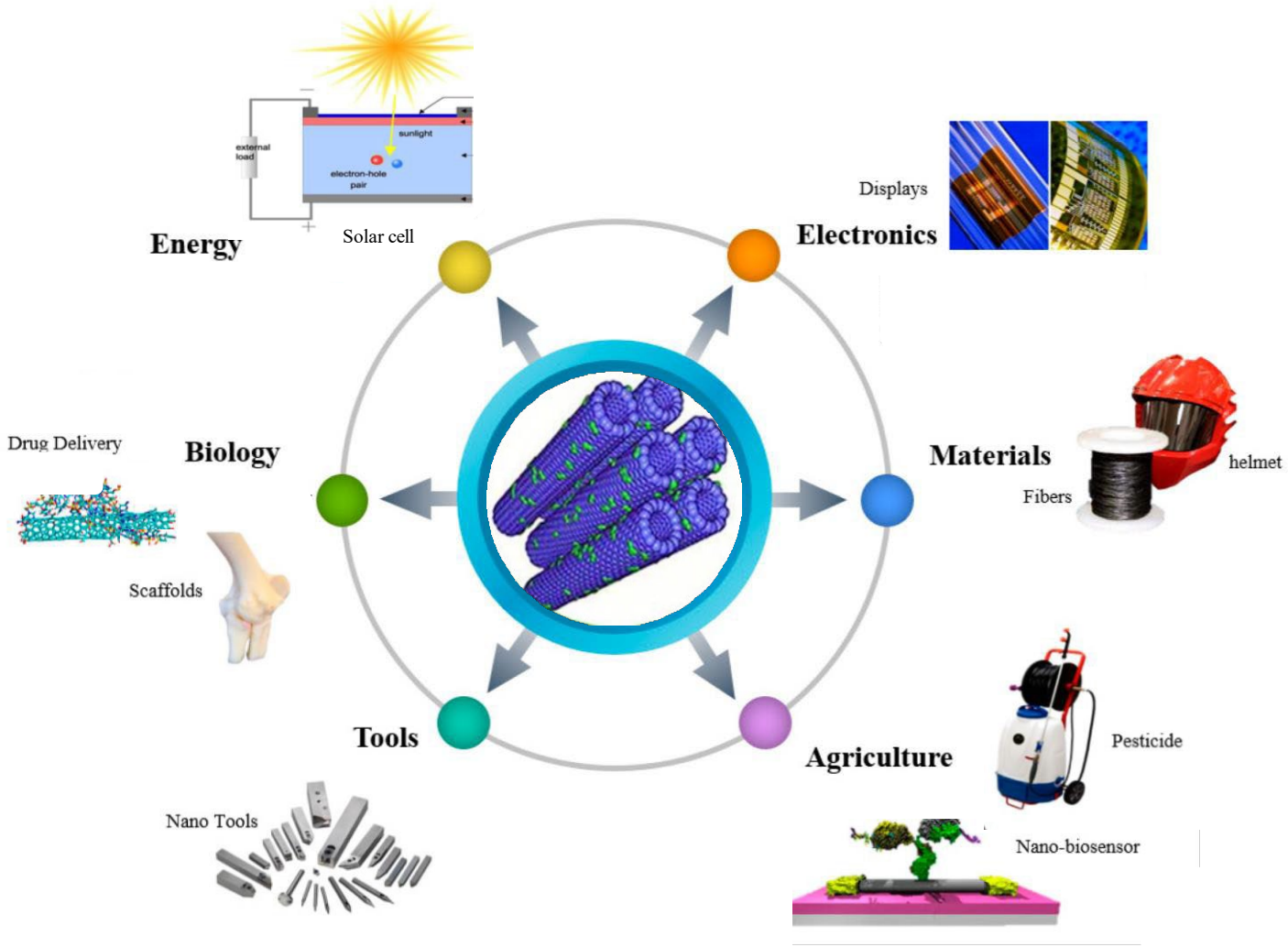


Dispersion matters!

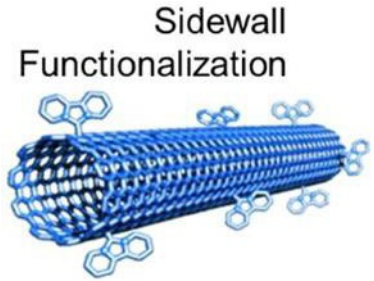
CNT agglomerates

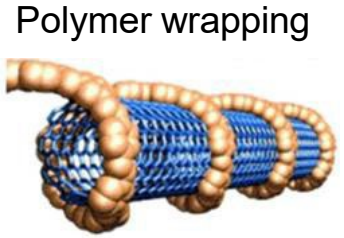
Kim et al., Nanomaterials 2012, 2(2), 206-216
Guo et al., ACS Appl. Mater. Interfaces 14 (14), 16809

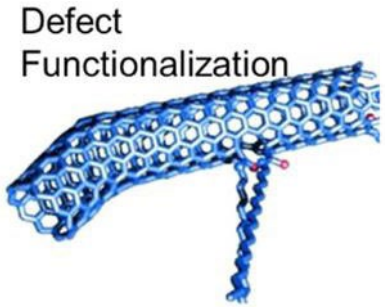
CNT dispersion in aqueous media is a critical step for processing and utilization

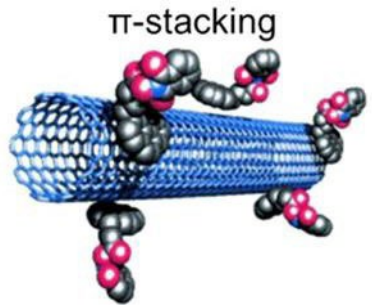


Possible solutions to the challenge of digestion:







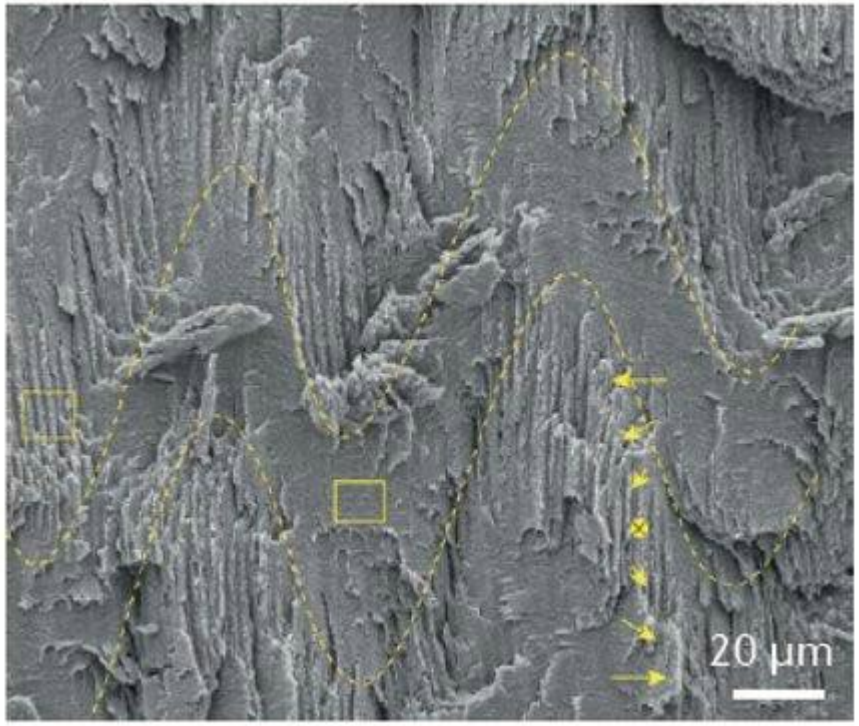


Others: **physical adsorption of biocolloids**

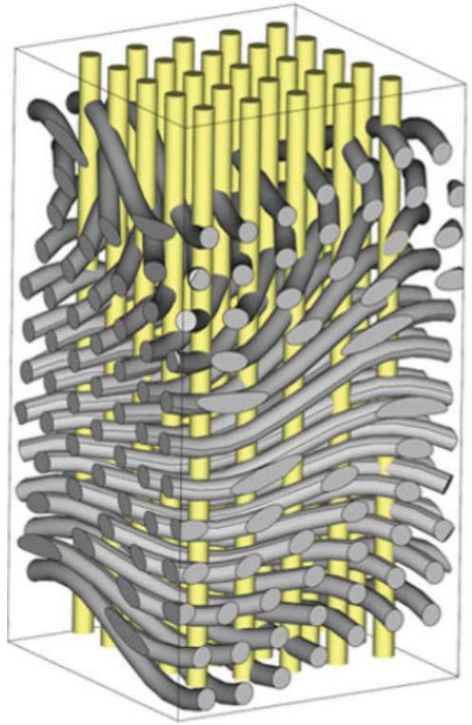
Hirsch et al., Angew. Chem., Int. Ed. 2002, 41, 1853.

Chitin nanocrystals: Unique oriented structure in nature

The snapshot of *Scyllarus*



SEM image of herringbone pattern



Highly oriented chitin nanofibrils

Cholesteric Structures in Biological Architectures - Fracture Dissipation

Weaver et al., *Science*, 2012, 336, 1275
Yaraghi et al., Adv.Mater.2016, 28, 6835–6844

Goal

Disperse CNT with nanochitin and adds to the mechanical features of final material

Strategy

1. Study disperse behavior

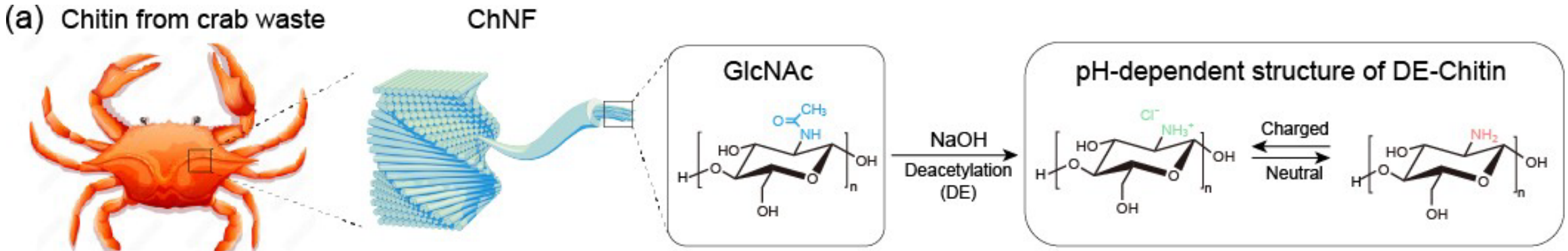
Optimization of binary system disperse condition by tuning:

- Nanochitin surface modification
- Protonation effects

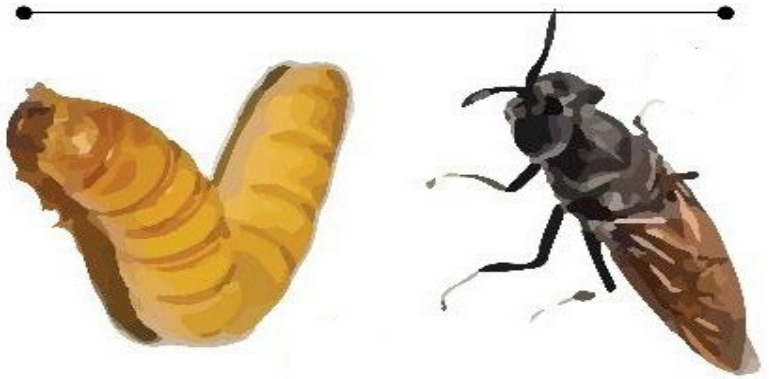
2. Fabricate material

Production of nanochitin/CNT composites using stable dispersion and explore its potential applications

Nanochitin is easily produced

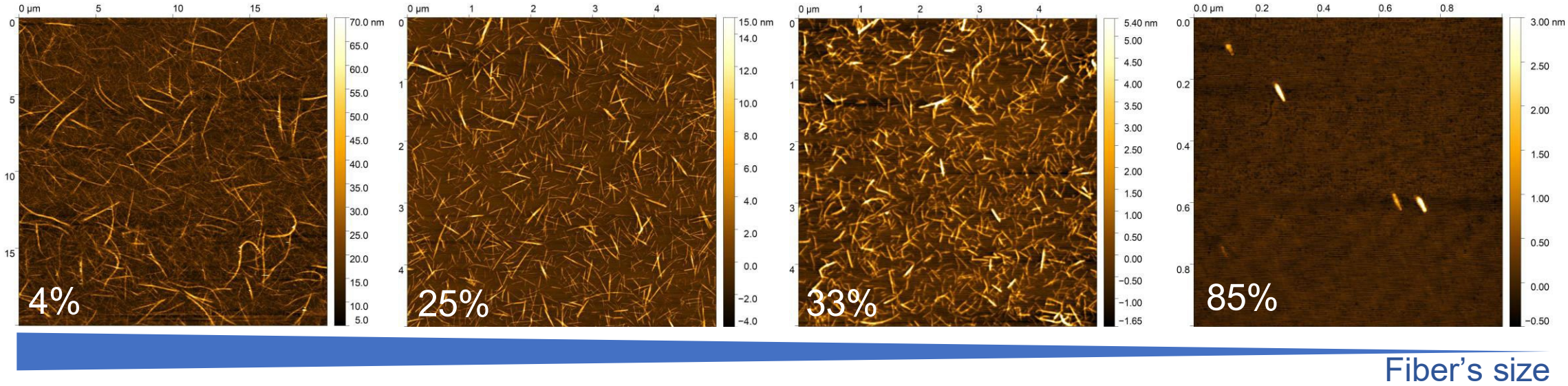


Residuals from shrimp, fly larvae, mealworm and fungi



Liu et al., ***ACS Nano*** 13, 2927 (2019)
Bai et al., ***ACS Sustainable Chem & Eng*** 7, 6497 (2019)

Nanochitin can be isolated with different sizes and degrees of deacetylation

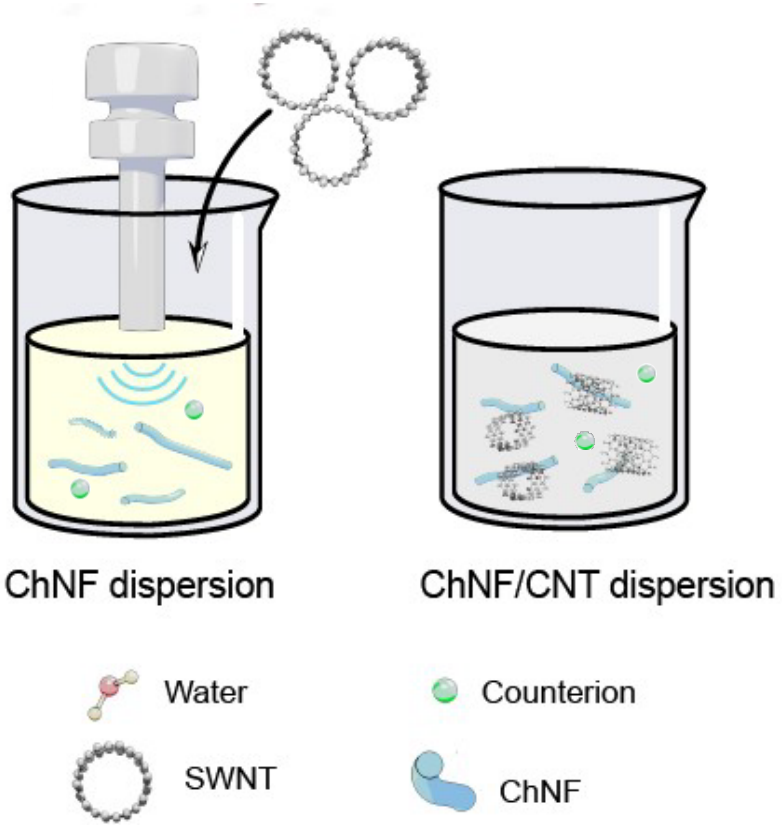


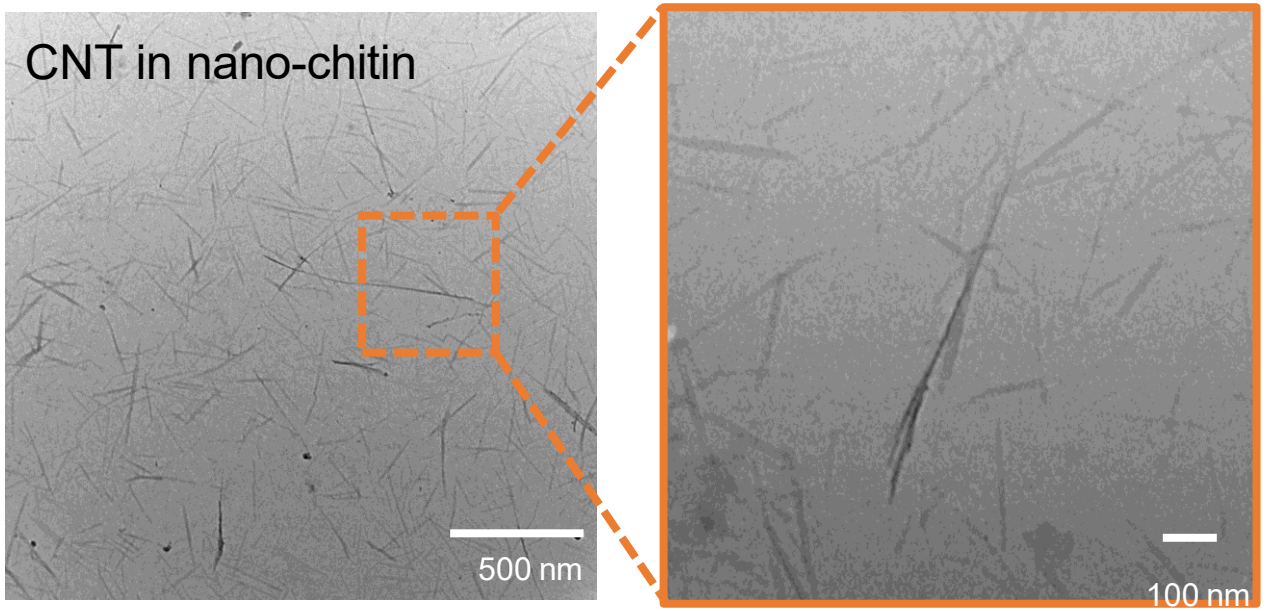
- **Degree of Deacetylation (DDA)** : 4%, 25%, 33% (commercial chitosan, 85%)
- Dimension: length: 50~2600 nm; width: 2~80 nm

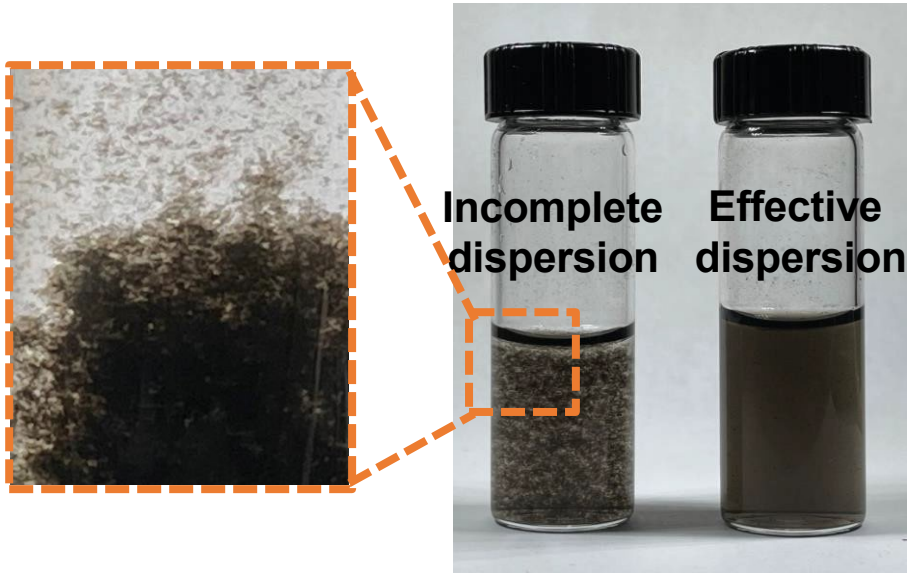
DDA	Length (nm)	Width (nm)
4 %	2500±100	80±5
25%	270±32	11±0.8
33%	169±20	5±0.7
85%	50±12	2±0.2

Effective dispersion of CNTs in aqueous nanochitin suspension

- Apply ultrasonic energy by sonicator
- Surface treatment with nano-chitin as a surfactant

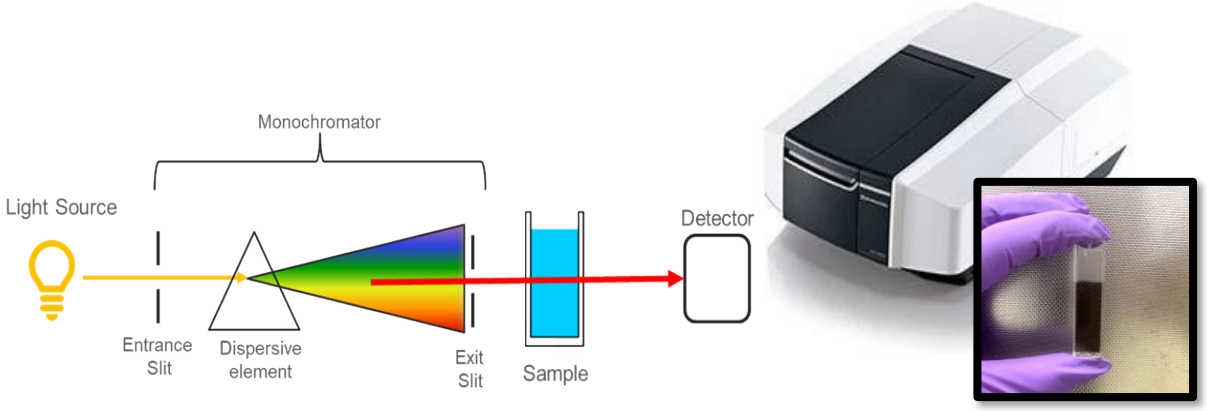






UV-VIS to study CNT dispersion (dispersion limit)

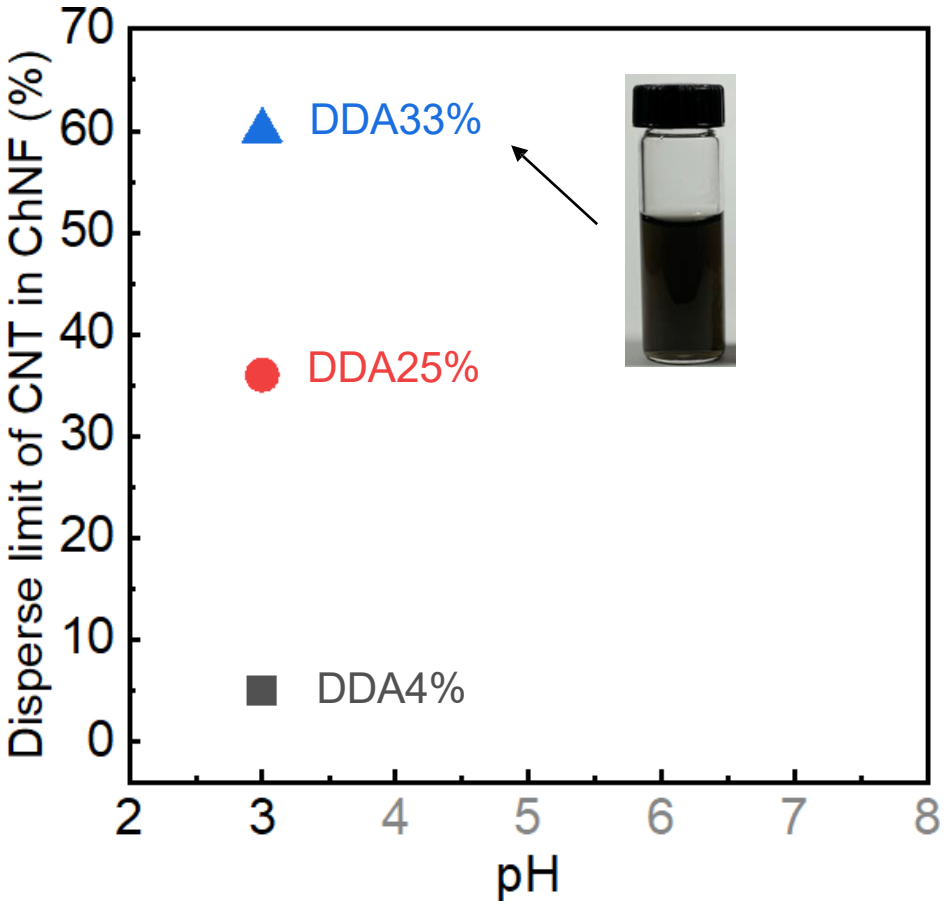
- Ultraviolet visible near infrared spectroscopy (UV-Vis-NIR)
- The disperse limit can be calculated by the UV result with the *Beer-Lambert Law*

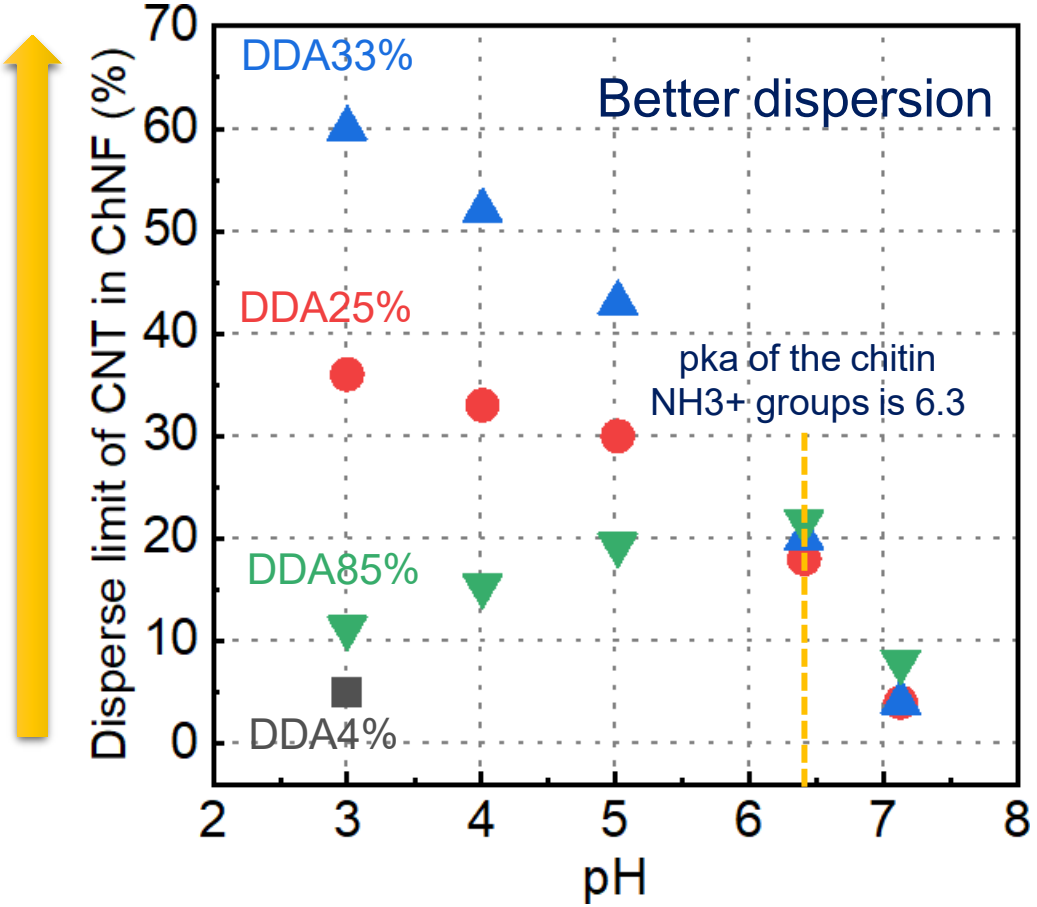


Supernatant of suspension after centrifugation

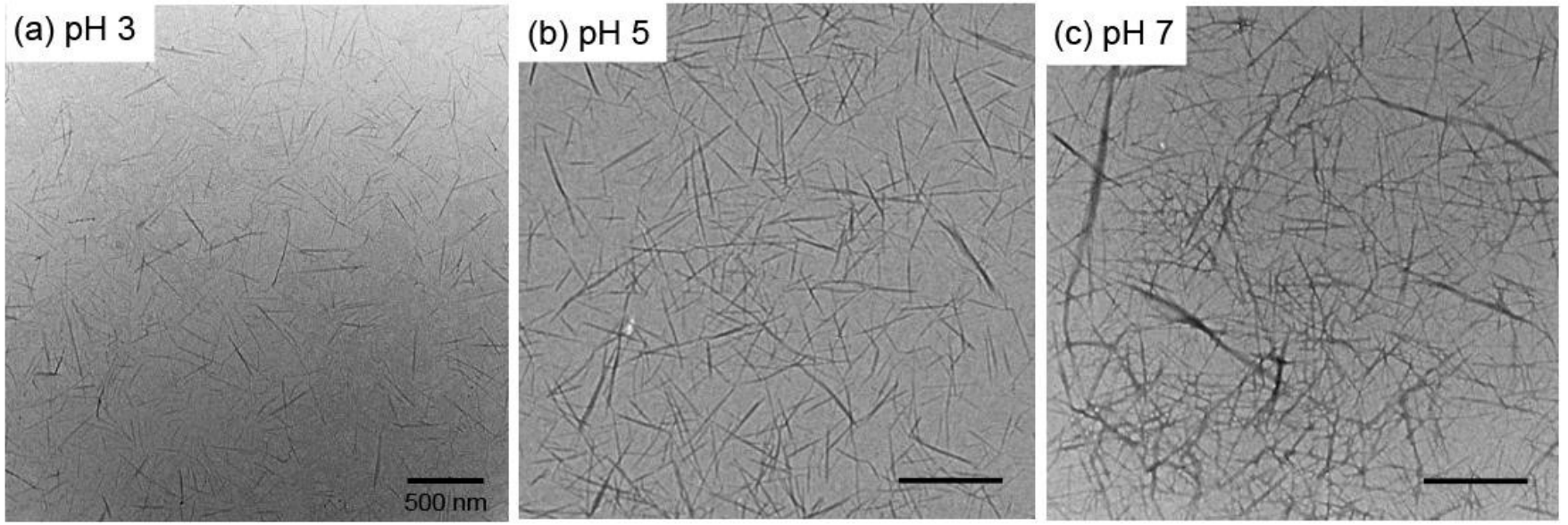
Low to high dispersion limit

Maximum disperse limit at intermediate DDA
A lower pH enables better SWCNT dispersion





Nanochitin (DDA= 25%) suspension at different pH

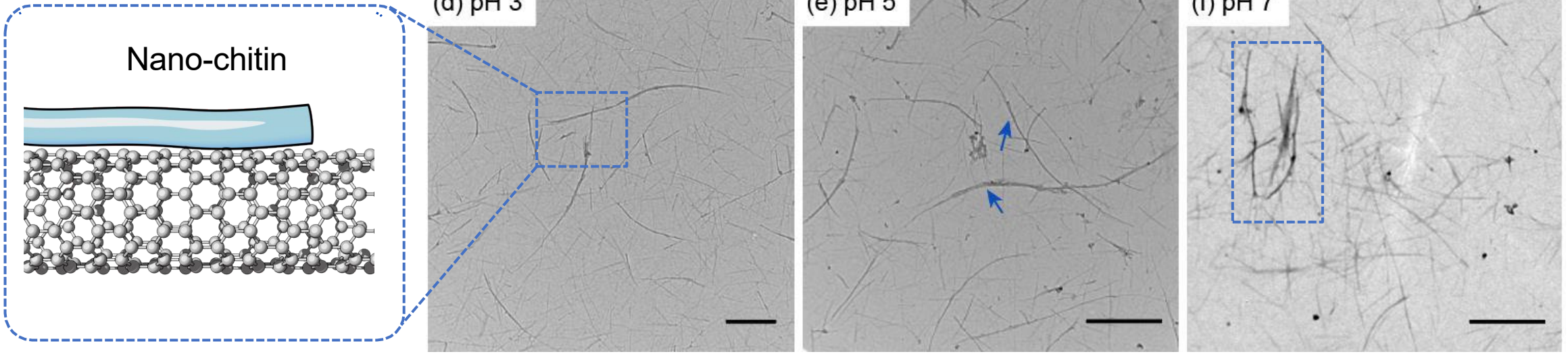


pH reduction

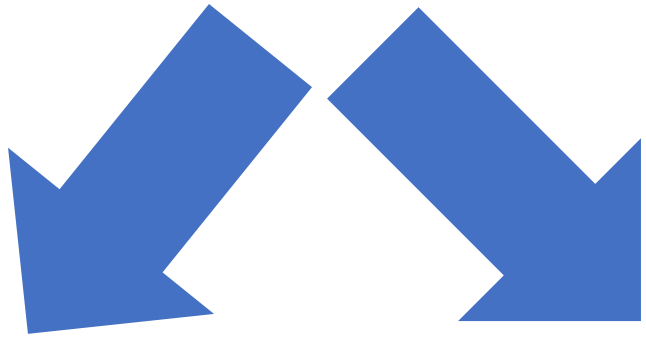
ChNF dispers

CNT

Nanochitin (DDA= 25%) suspension with added CNT at different pH



Microscopy/spectroscopy cannot establish the relationship between the state of CNT dispersion and distribution in a matrix (nano-chitin)

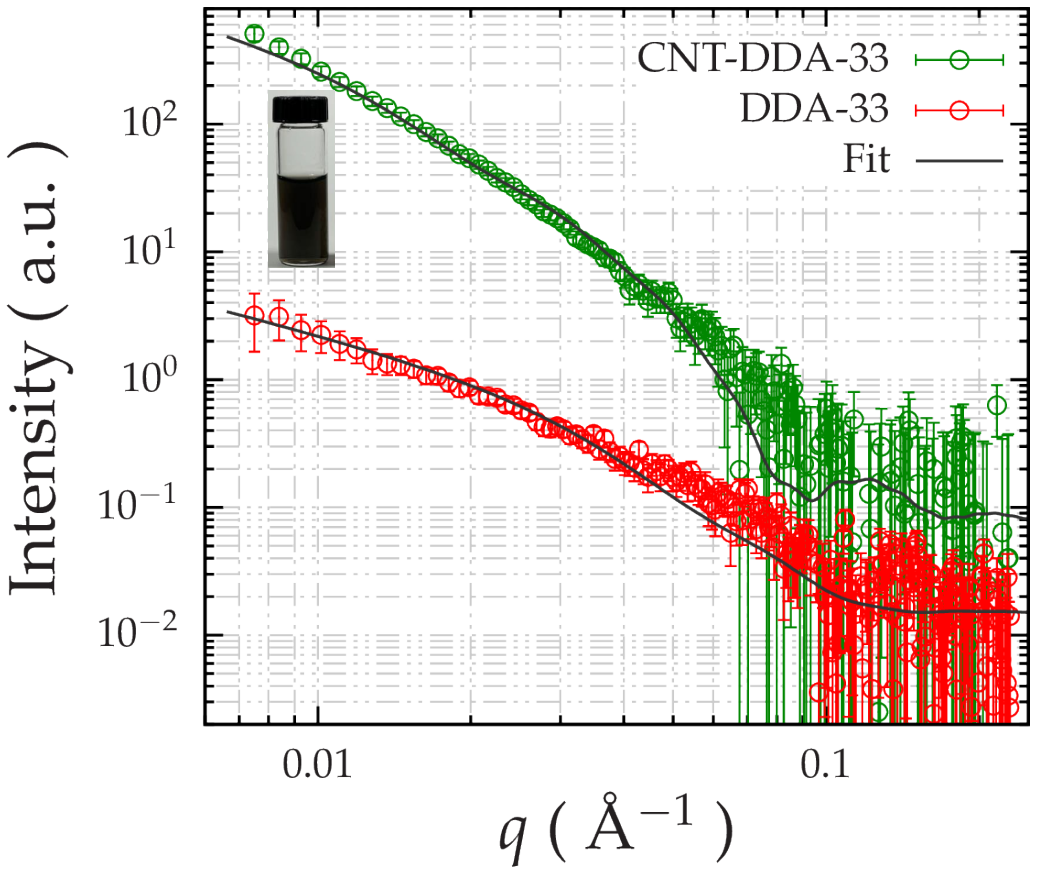


Small angle X-ray scattering

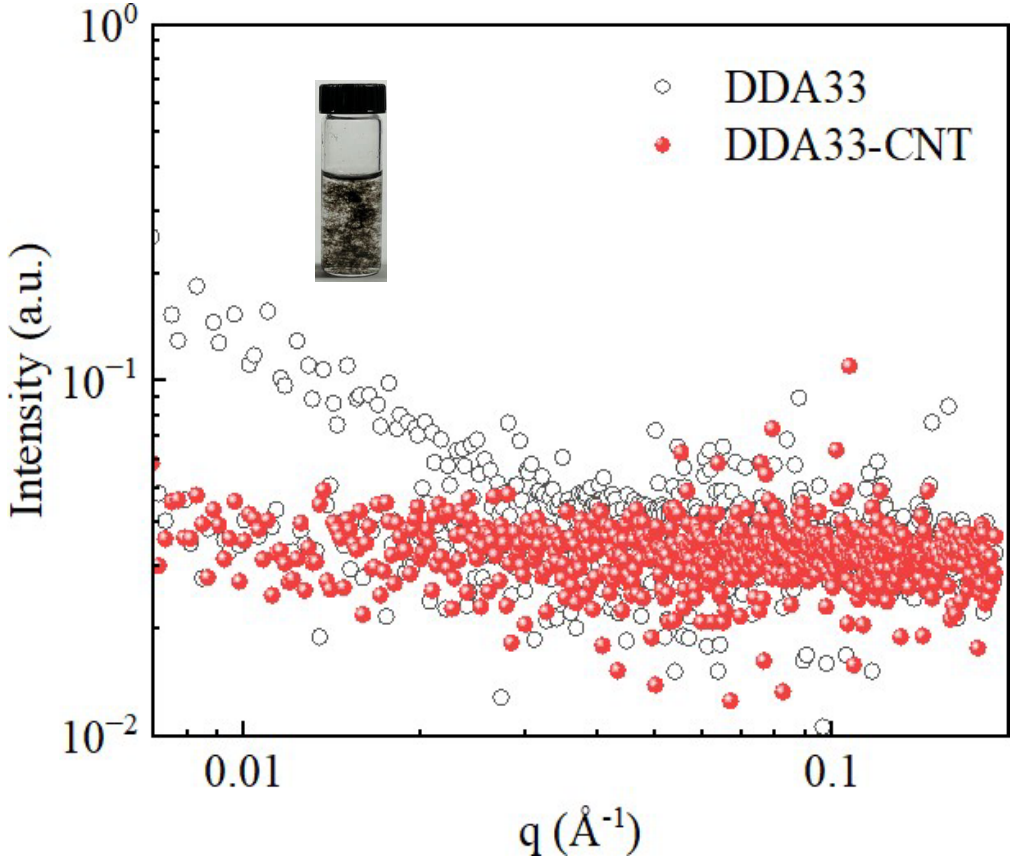
Molecular simulation

Small Angle X-ray Scattering

pH=3



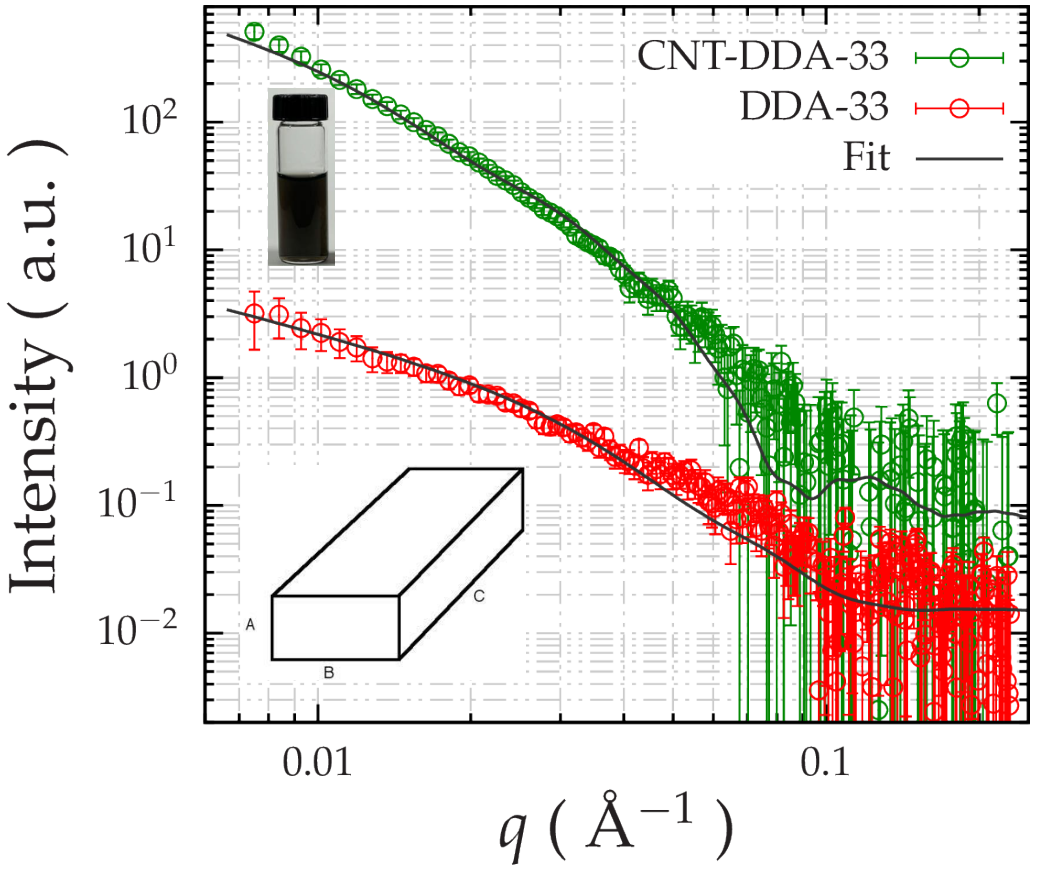
pH=7



The aggregation leads to bad scattering sampling.

Small Angle X-ray Scattering

pH=3



Rectangular parallelepiped (random orientation)

$$I(q) = \frac{\text{scale}}{V}(\Delta\rho \cdot V)^2 \langle P(q, \alpha, \beta)\rangle + \text{background}$$

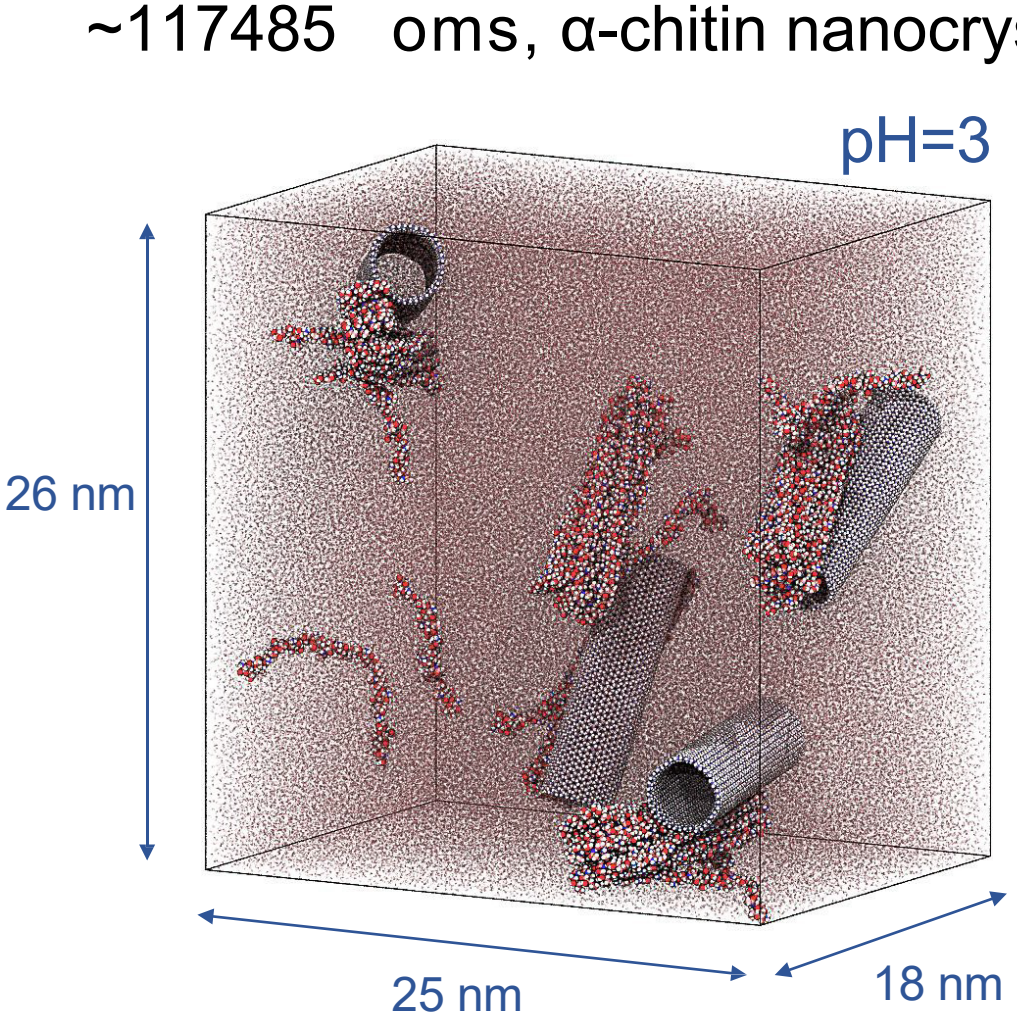
	pH3		pH5	
	DDA33	DDA33+CNT	DDA33	DDA33+CNT
Rg (Å)	79	194	75	244

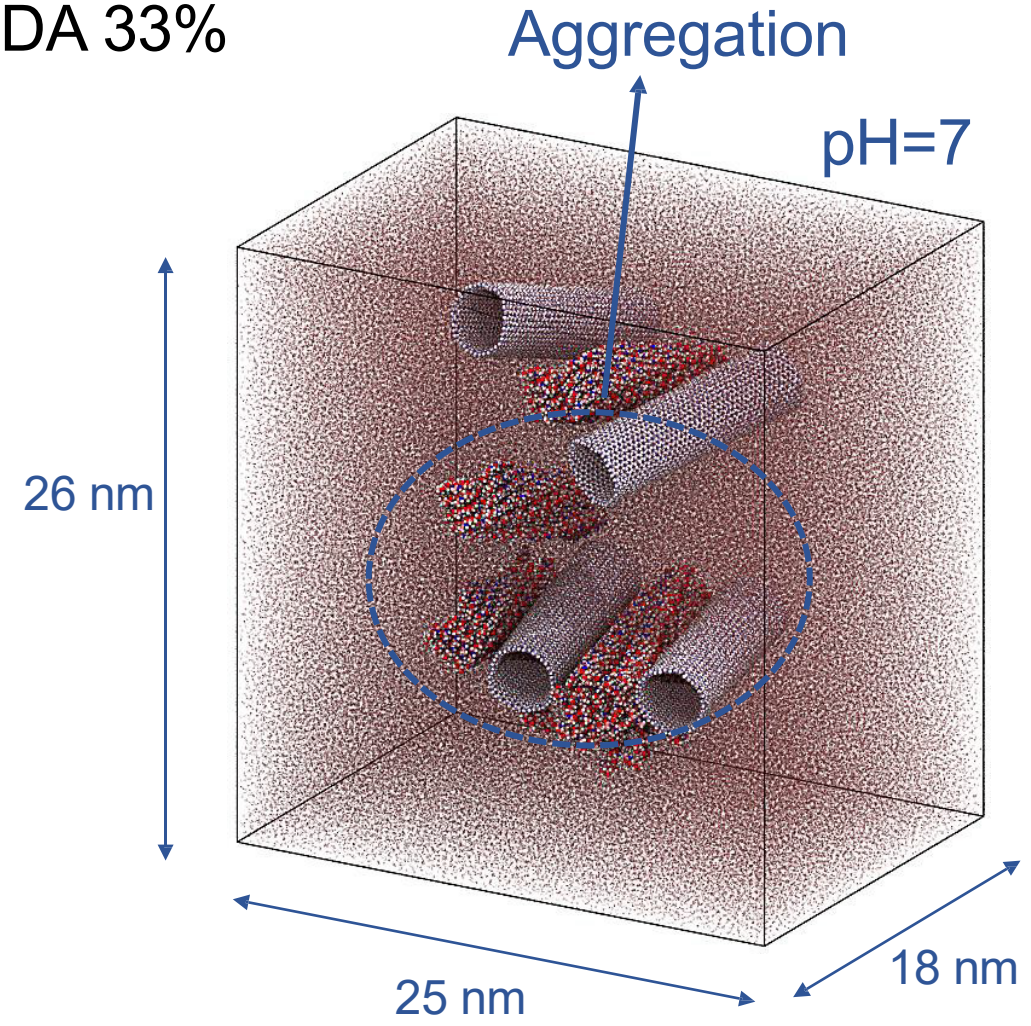
CNT addition: the radius of gyration (Rg) of particle increased due to the absorption between CNT and ChNF.

P Mittelbach and G Porod, Acta Physica Austriaca, 14 (1961) 185-211
R Nayuk and K Huber, Z. Phys. Chem., 226 (2012) 837-854

Simulation structure of Nanochitin dispersing CNT

~117485 oms, α-chitin nanocrystal with DDA 33%



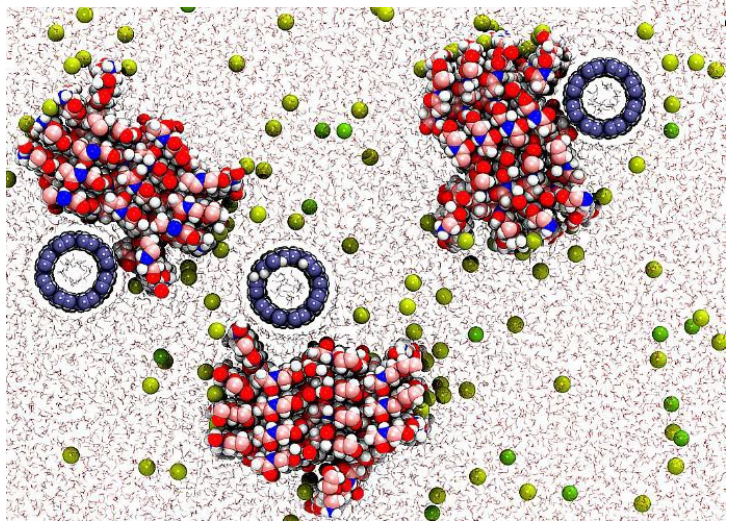


Method: Annealing from 298.15 K to 333.15 K, simulating at 333.15 K for 2ns, cooling from 333.15K to 298.15K

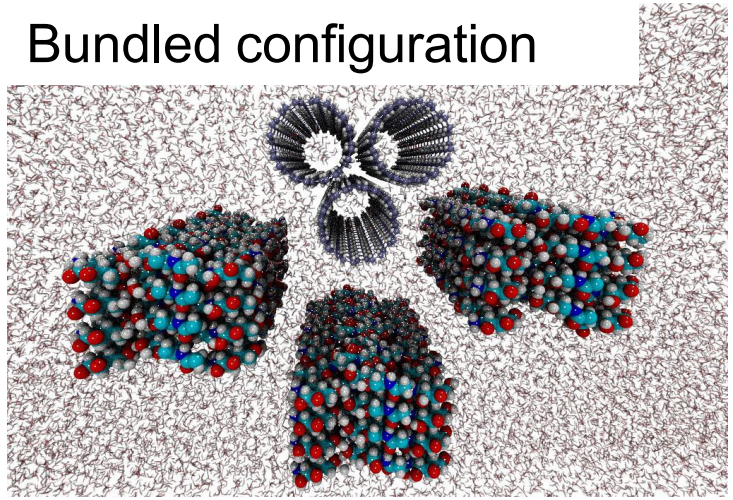
Suter et al. Advanced Materials (2020)

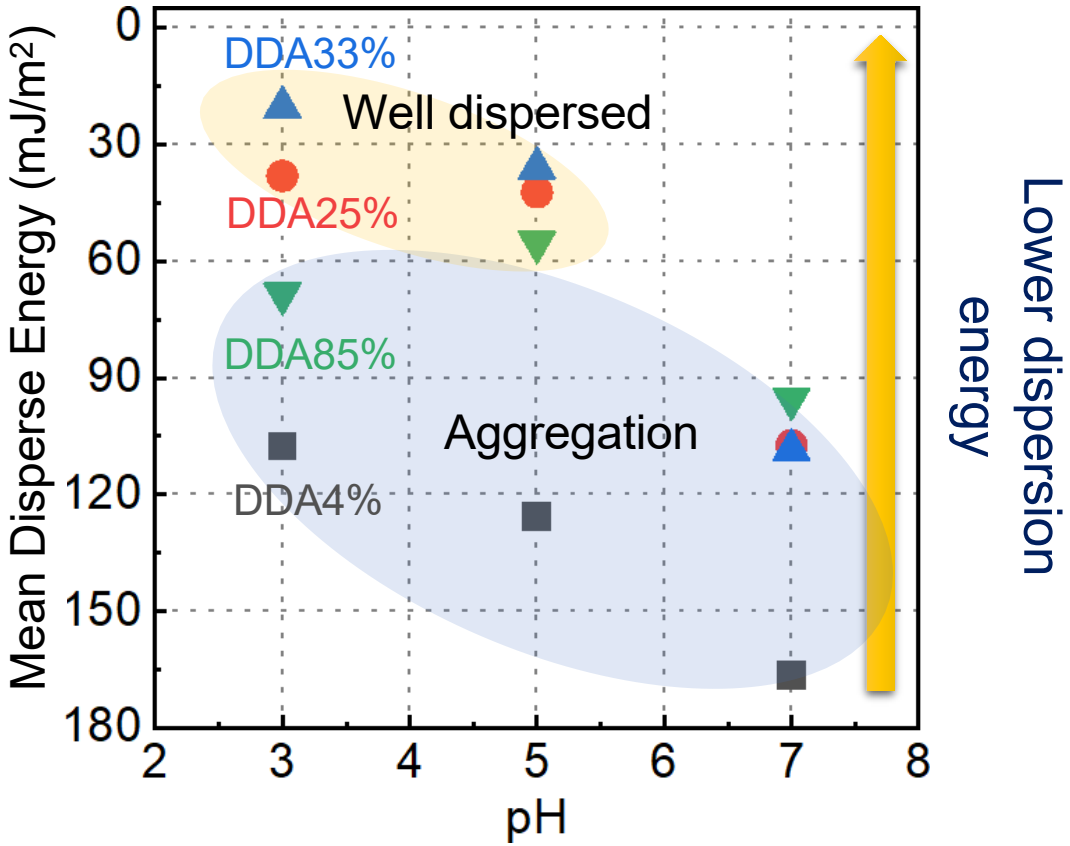
Simulation - dispersion energy

Dispersed configuration



Bundled configuration



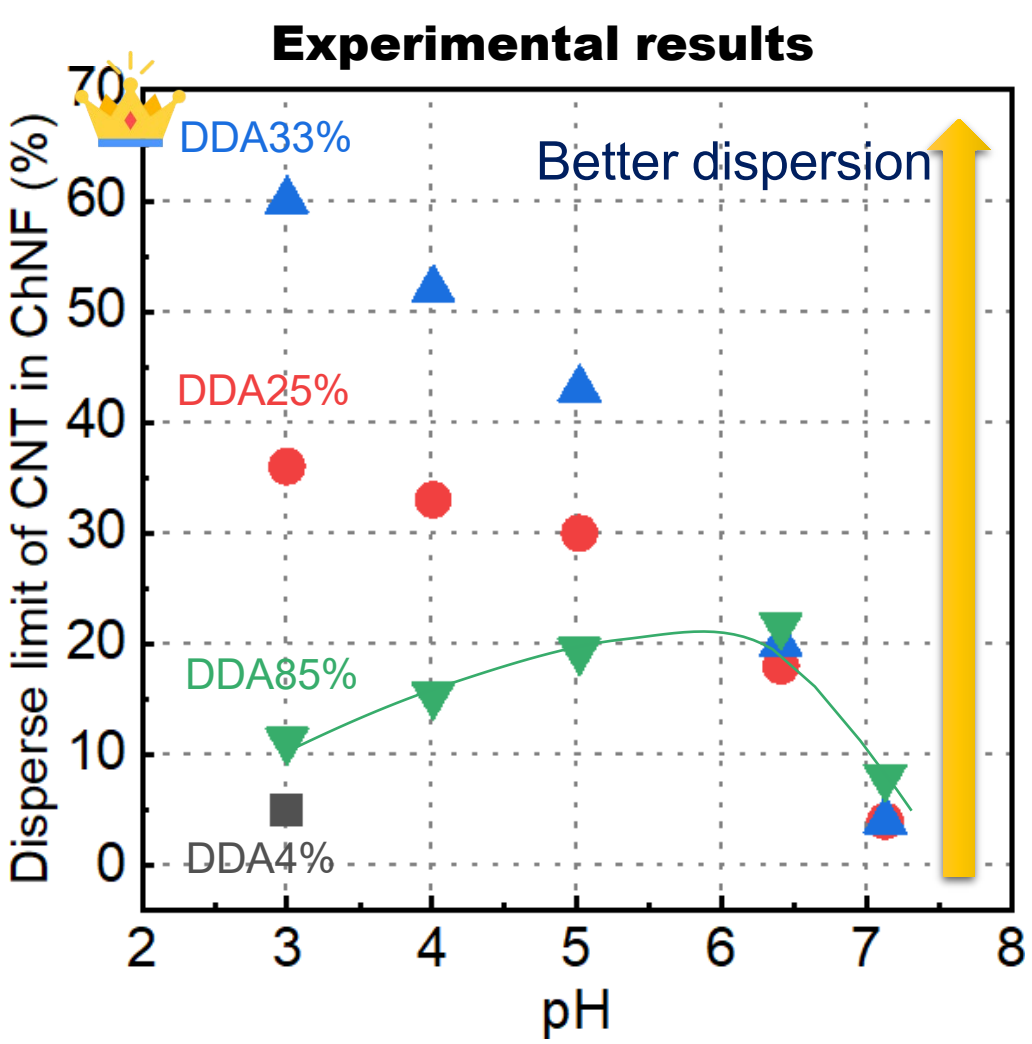


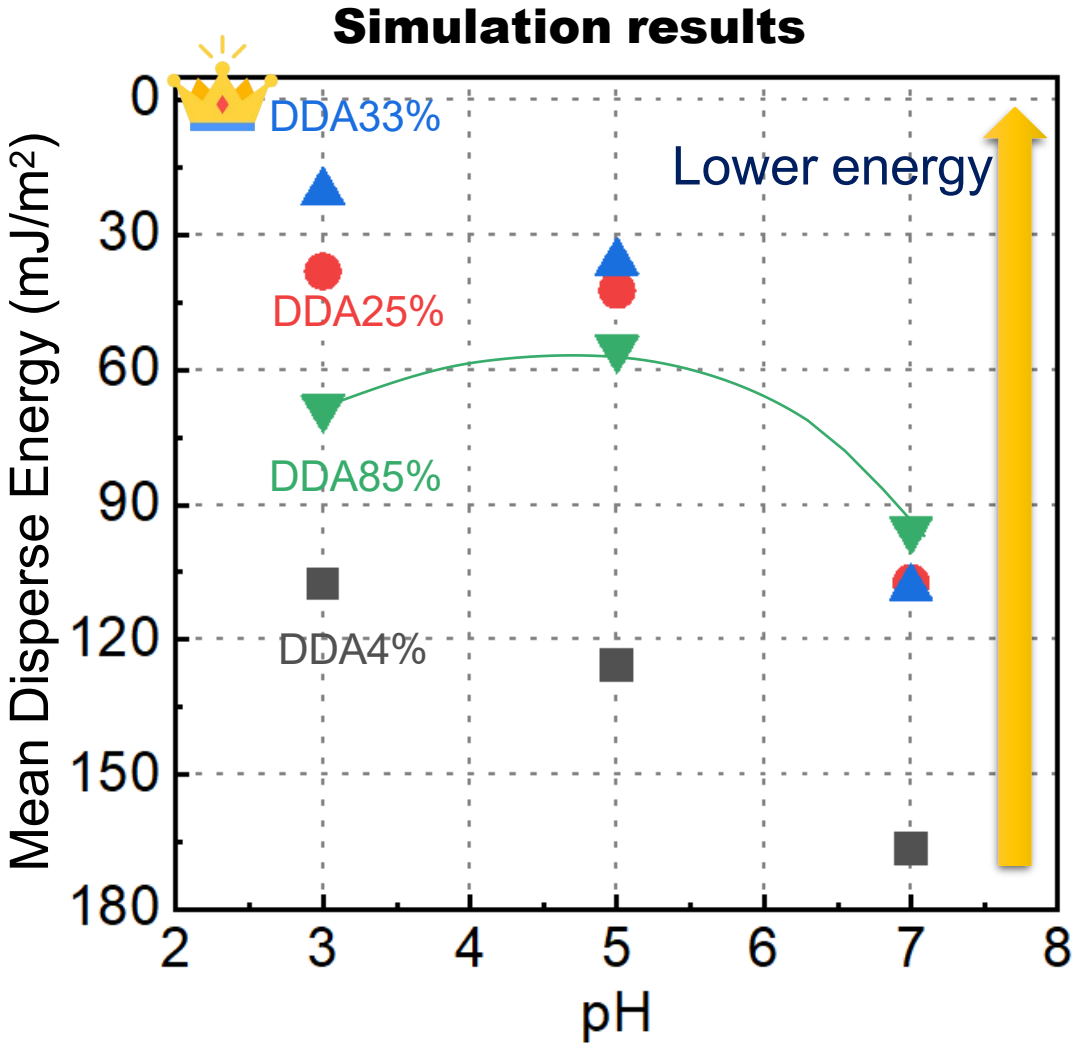
ΔE(is ersio e er)=ΔE(is erse)-ΔE(b es)
(Two-box method)

CNTs in vacuum environment: 175 mJ/m²;
CNTs in chitin: 20 mJ/m²

Heinz et al. Journal of Computer Chemistry (2010)

Comparison of experimental and simulation results





Goal

Disperse CNT with nanochitin and adds to the mechanical features of final material

Strategy

1. Study disperse behavior

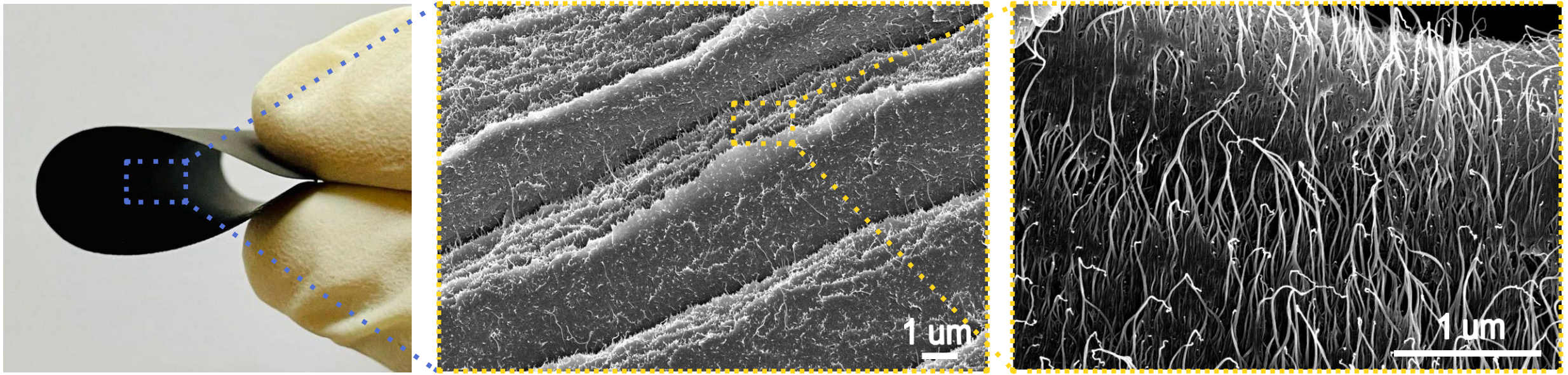
Optimization of binary system disperse condition by tuning:

- Nanochitin surface modification
- Protonation effects

2. Fabricate material

Production of nanochitin/CNT composites using stable dispersion and explore its potential applications

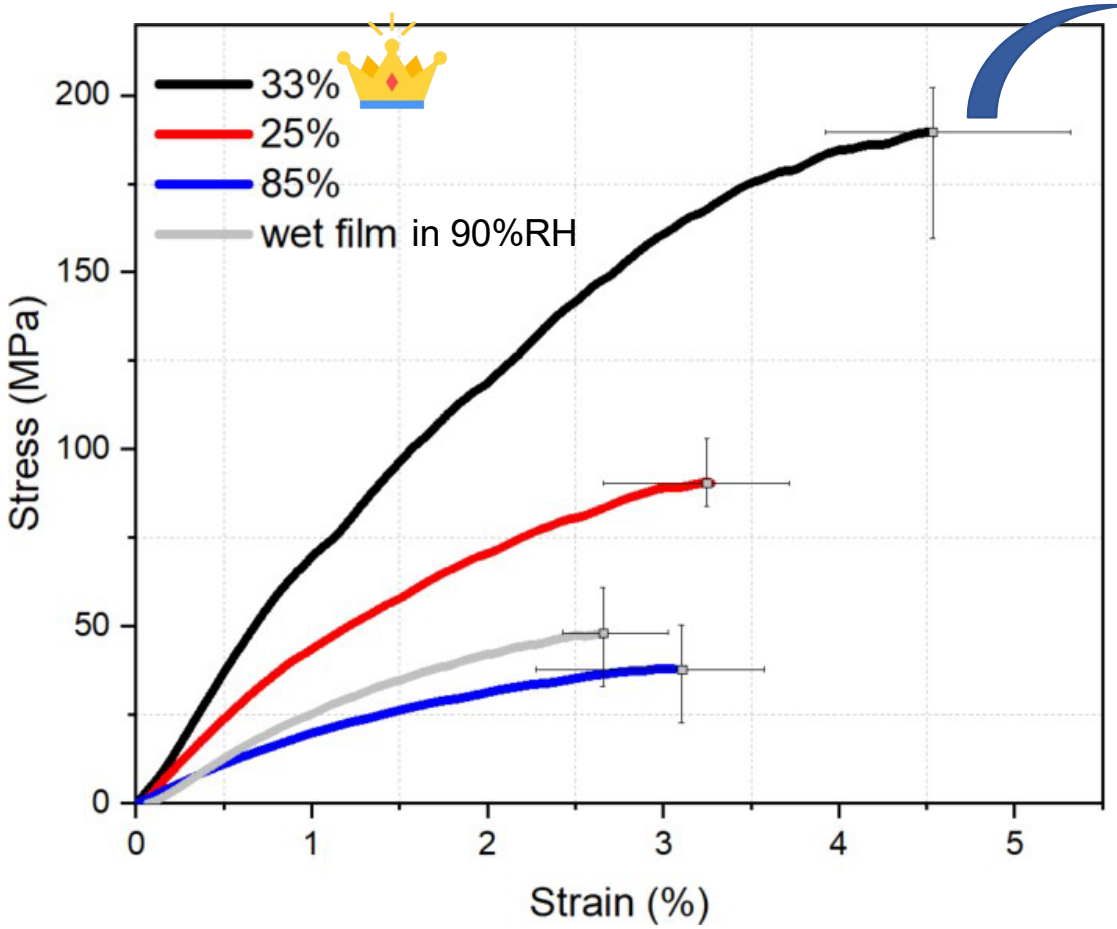
Assembly of CNT and nano-chitin fibers



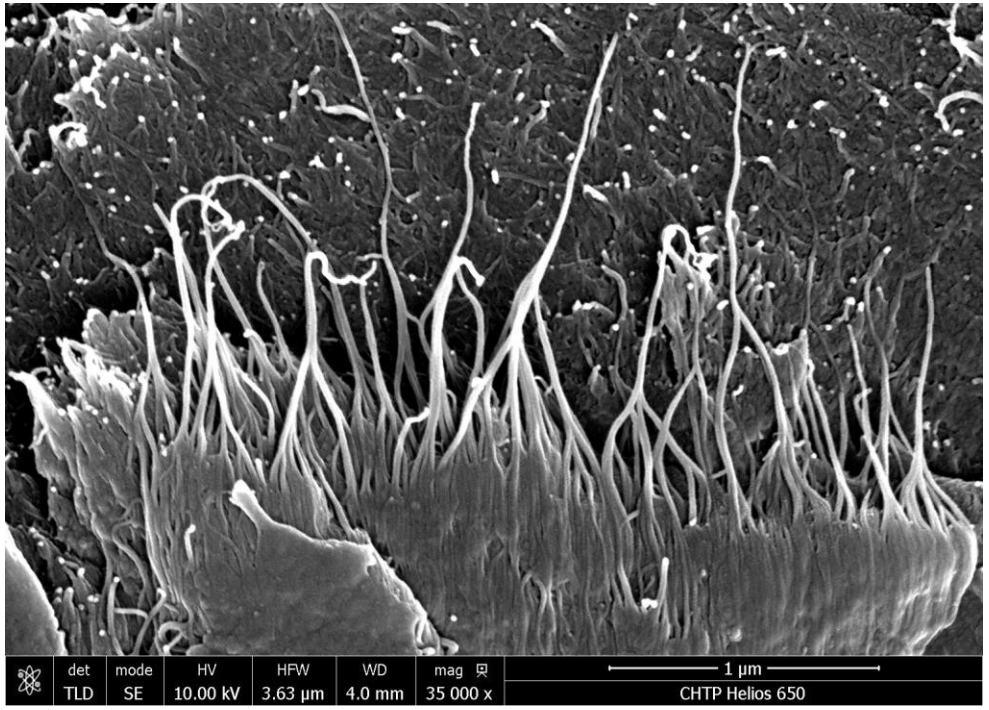
The CNT is well embedded into fibrous chitin network.

Optimum DDA (33%) for dispersion gives best mechanical strength

50/50 w/w composite films with different DDA



SEM of stretched film shows ductility



Recyclable/reusable

Hot pressing

Immersion

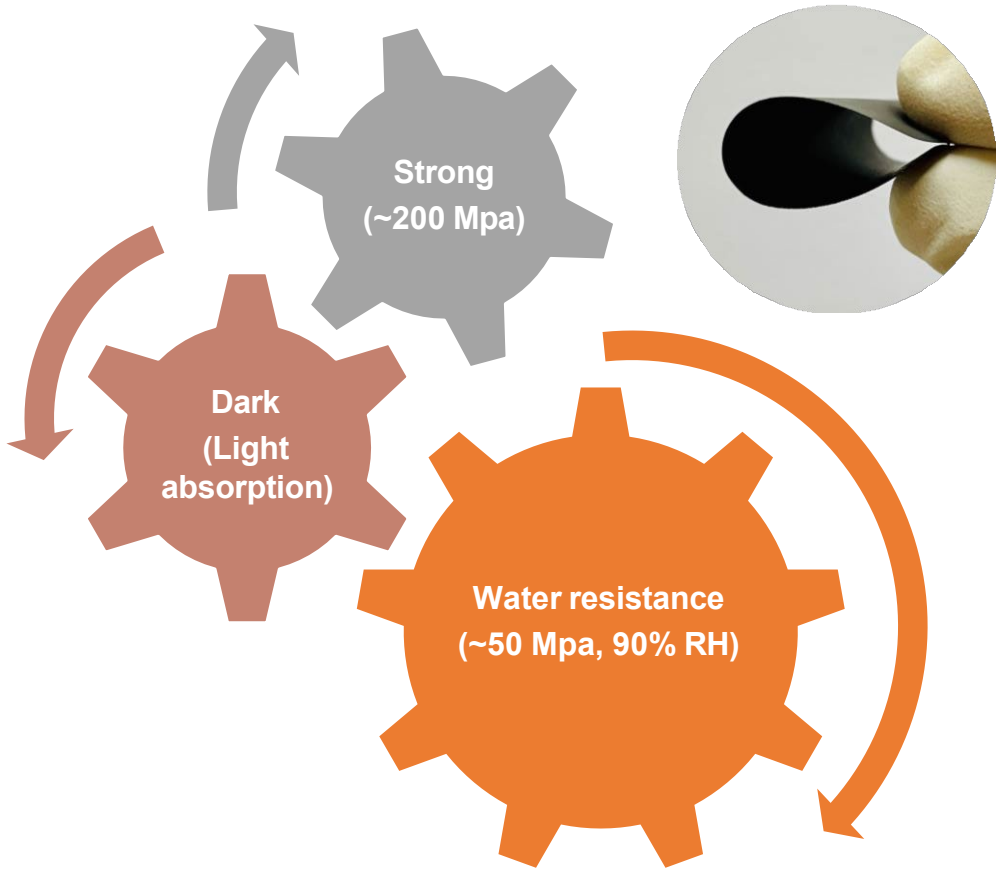
30 min

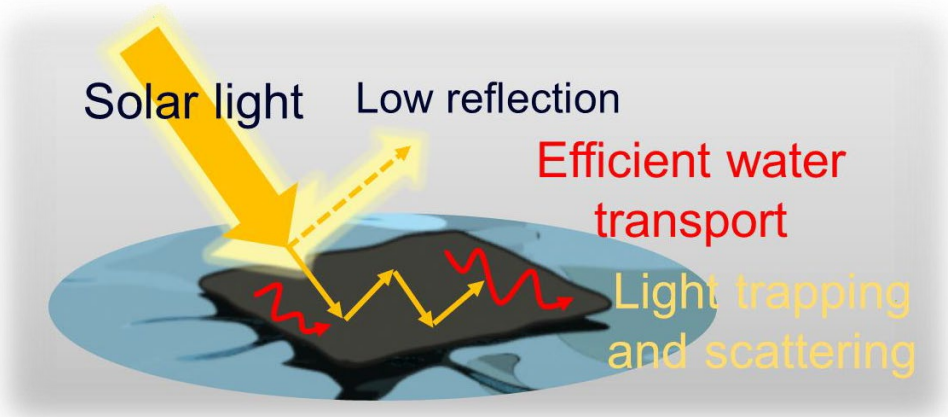
stir

1 min

Vacuum filtration
or casting

Utilization of thin film for solar evaporation

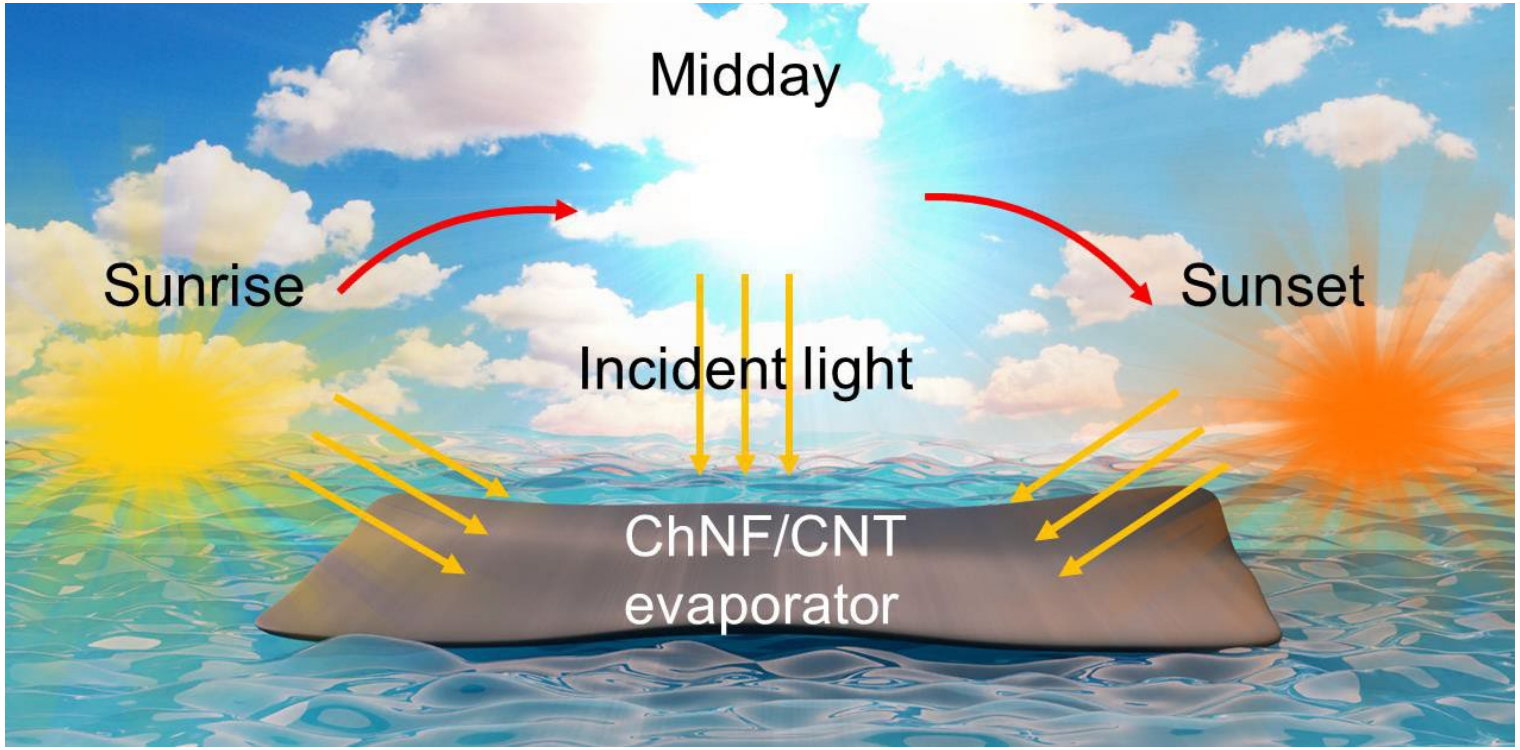




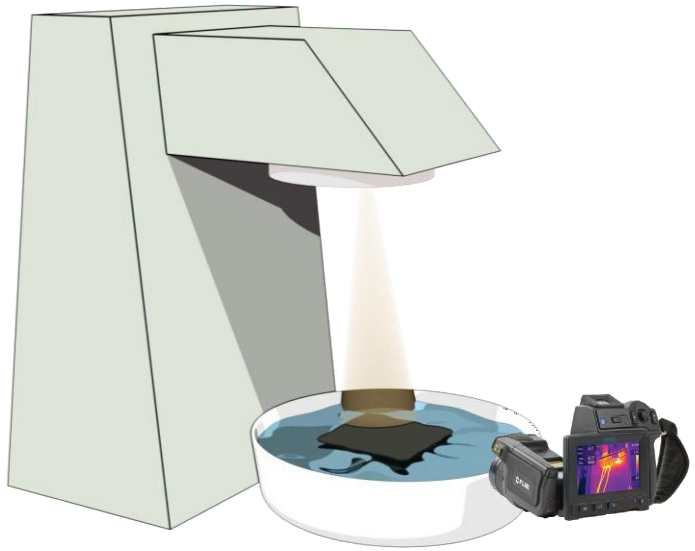
Photothermal conversion on ChNF/CNT nanopaper surface

Hierarchical photothermal evaporator

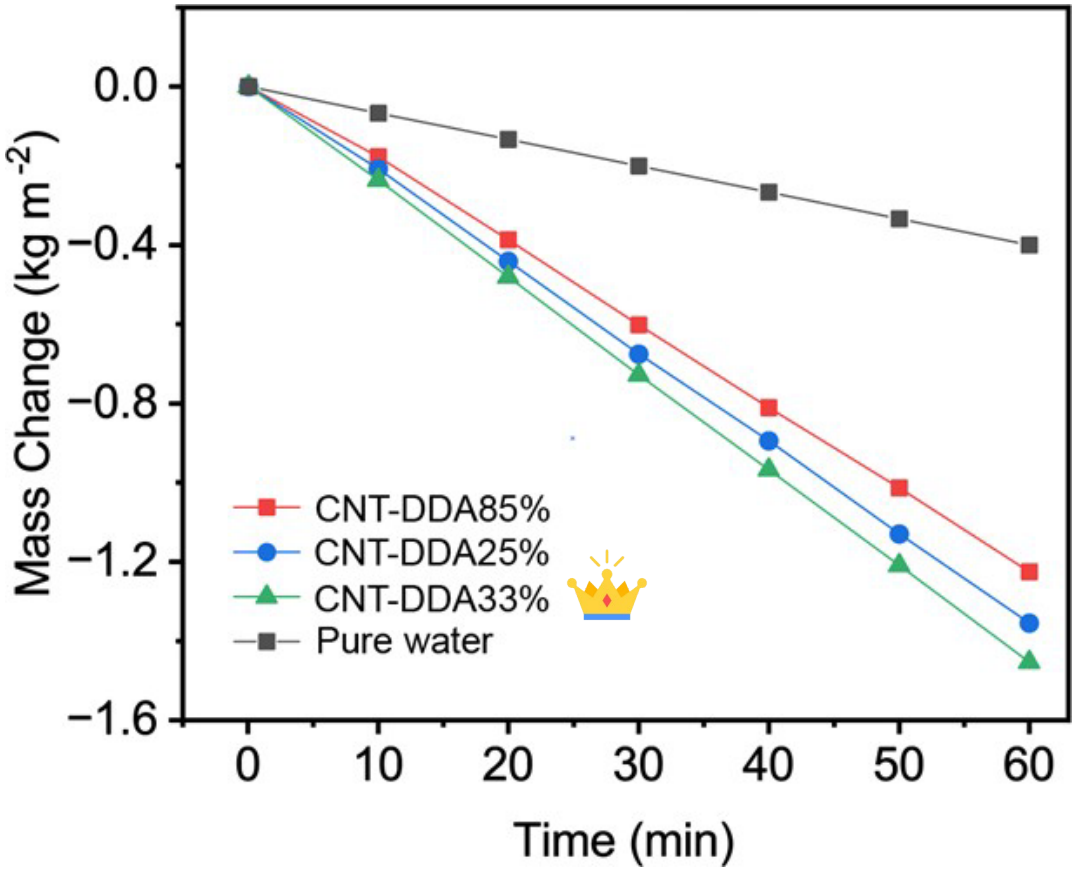
- An attractive technology for water purification and energy harvest;
- Advantage of ChNF/CNT film: water resistant, sustainable, strong, durable



Better dispersion leads to higher energy absorption

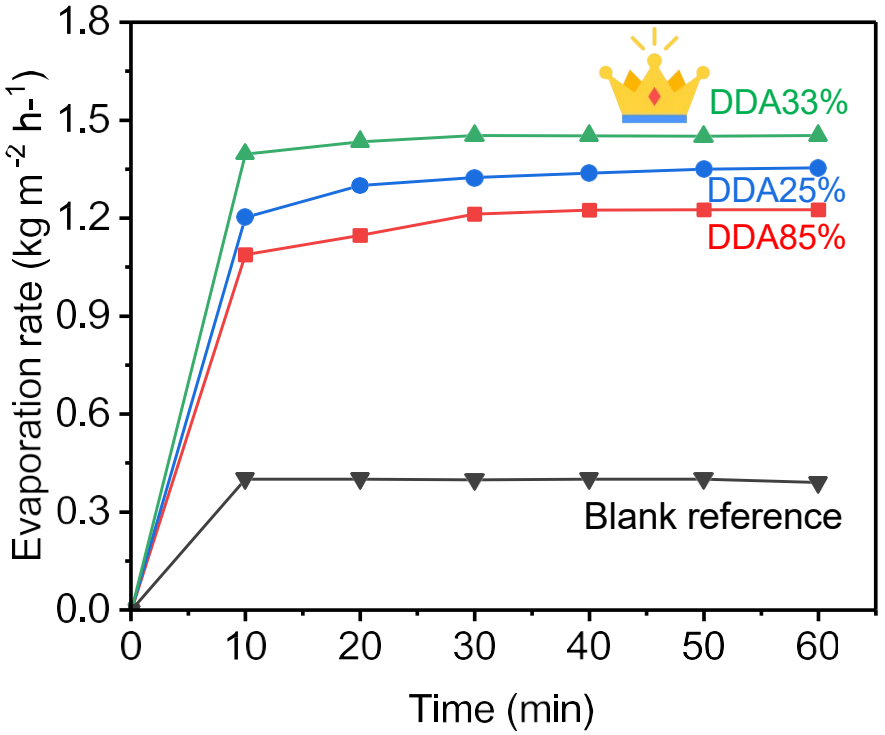


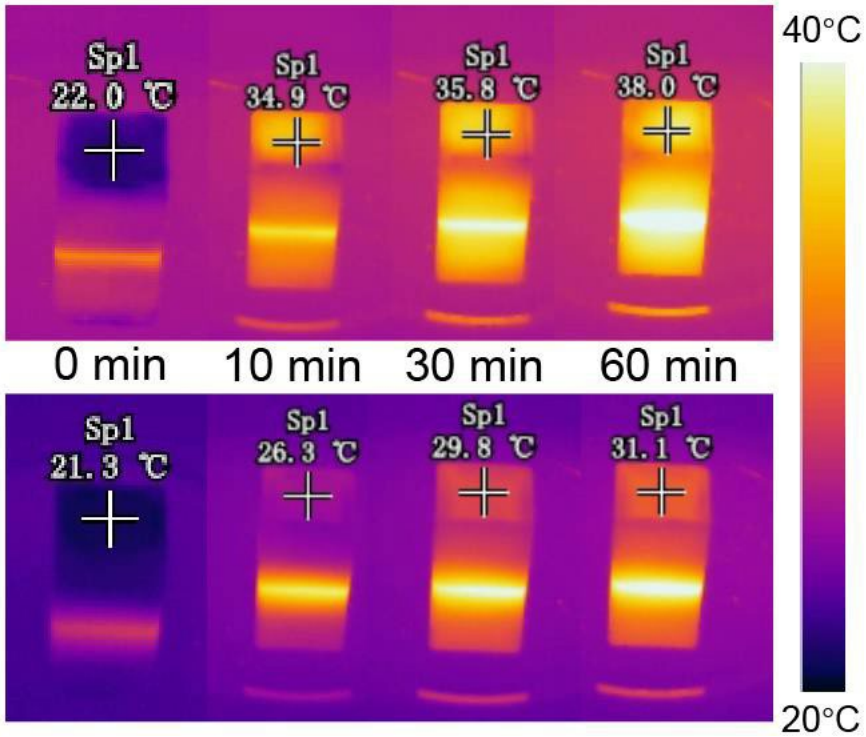
Evaluation of the solar evaporation



The thin films can be utilized for photothermal evaporation, water steam harvest and sea water desaltization process

Better dispersion leads to higher energy absorption

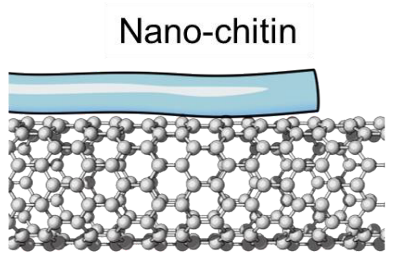


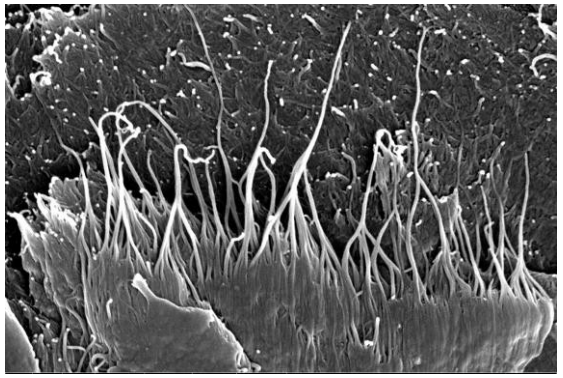


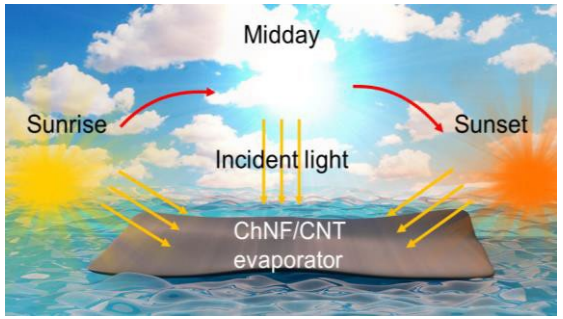
- The water evaporation depends on SWCNTs/ChNF assembly in the thin films;
- SWCNTs/nano-chitin film enhances the light absorption (incident light trapping and reflection reduction)

Summary

- UV-Vis-NIR can be used to assess the degree of CNT dispersion in aqueous nanochitin suspensions;
- To investigate the dispersion state of CNTs in nano-chitin matrix, SAXS and MS is applied which provide valuable information on how actual CNT dispersion is affected by chitin configuration (DDA and pH);
- Well dispersed composite thin film is mechanically stable in humidity environment, which is proposed to be used for solar evaporator.







Acknowledgements

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Dr. Gabriel Banvillet, Dr. Yi Lu

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