Aalto University
School of Chemical
Engineering

Nanocellulose Liquid Crystal Bubbles, Emulsions and Colloidal Glass

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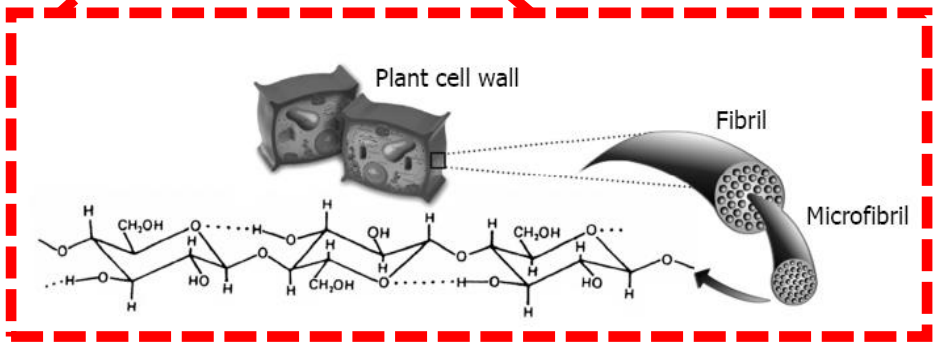
TAPPI Nano 2021 Virtual Conference
15-16 June 2021

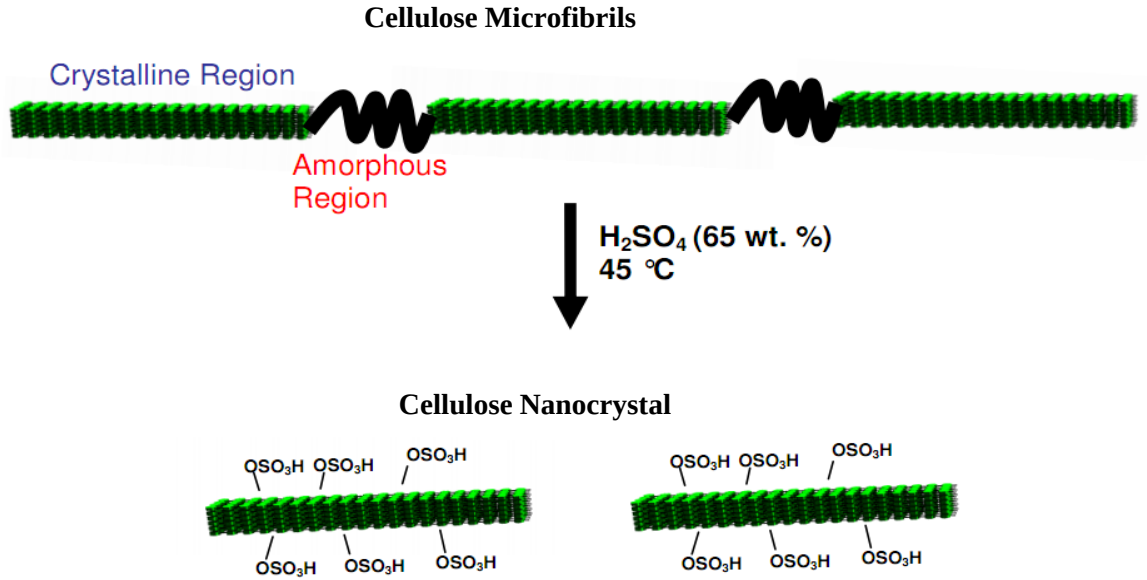
From Cellulose to Cellulose Nanocrystals (CNC)

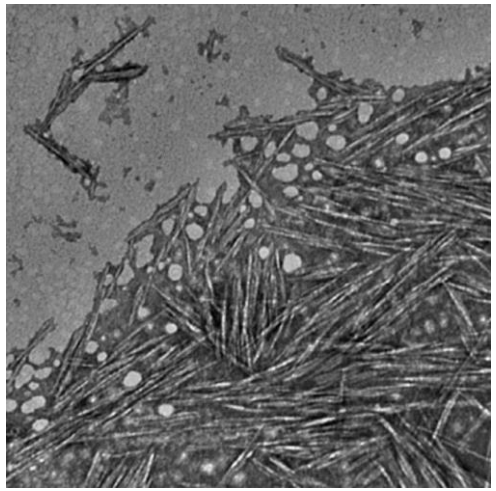
Wood, Cotton, Bacterial…



- Cellulose: linear chain of linked D-glucose units
- Most abundant, biocompatible, biodegradable
- Renewable biopolymer
- Clean Production

Preparation of cellulose nanocrystal





Cellulose Nanocrystal:
Twisting Morphology
Length: 200-400 nm
Diameter: 15-20 nm

Discuss. Faraday Soc. **1951**, *11*, 158-164

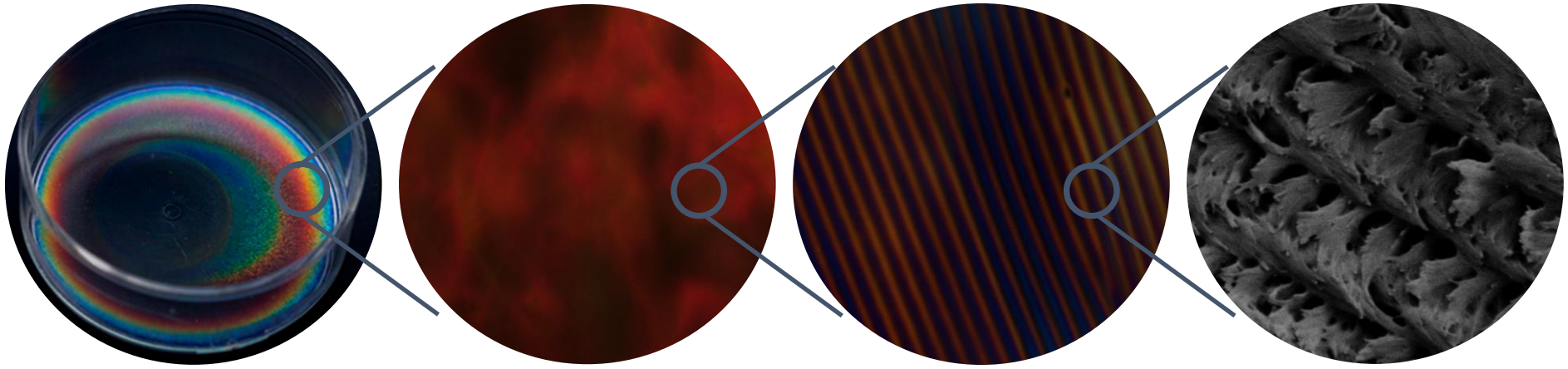
Cellulose Nanocrystals for Self-assembly

Phase separation

Isotropic phase

Anisotropic phase

Self-assembly for chiral photonics

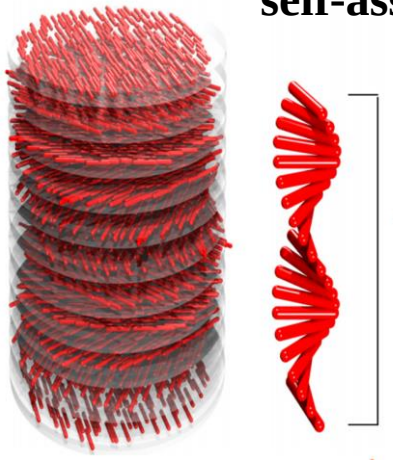


Drying induced self-assembly

Structural color

Long-range fingerprint texture

Short-range helical arrangement



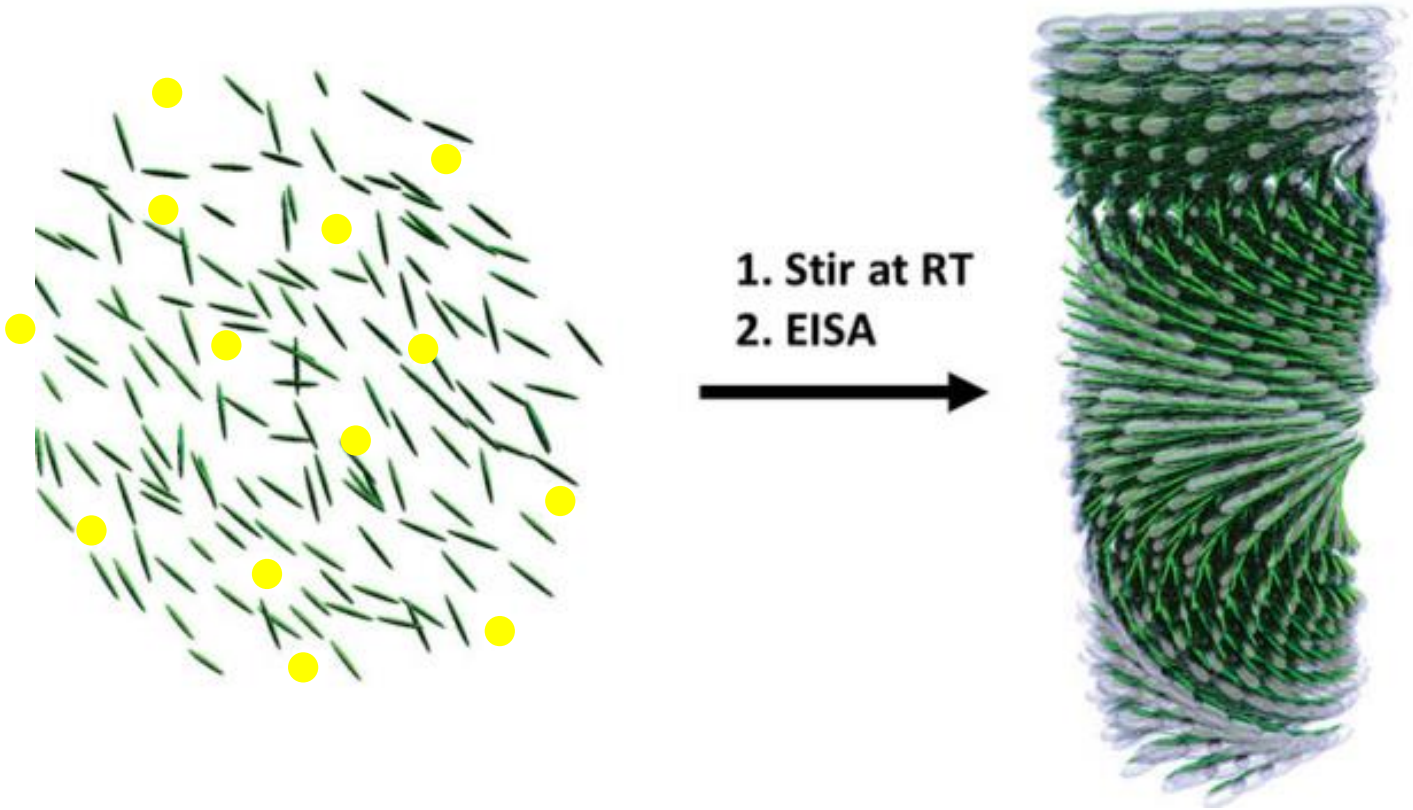
Cholesteric organization

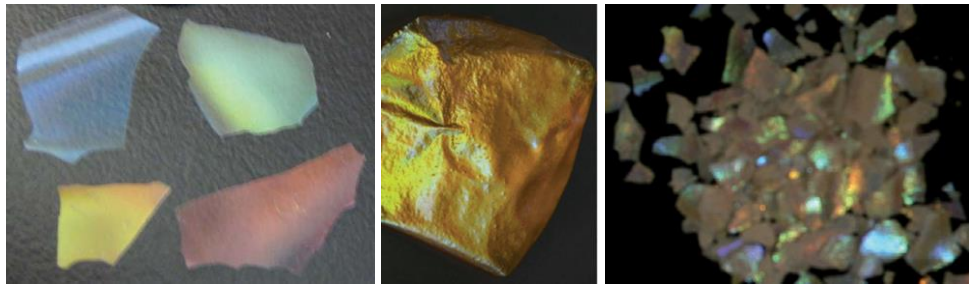
Cellulose Nanocrystal: CNC

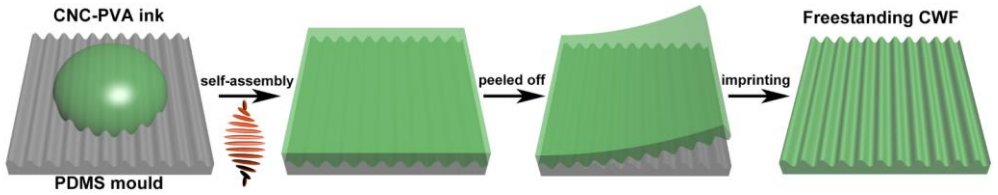
J. Pulp. Pap. Sci. **1998**, *24*, 146-149

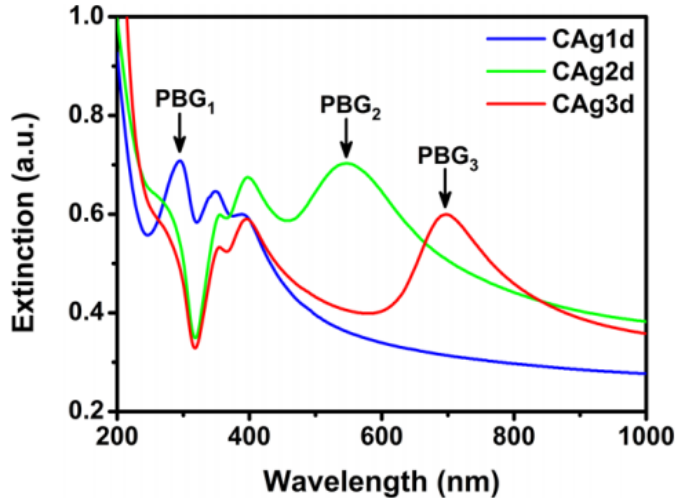
Current Research Progress and Strategy

Evaporation Induced Self-co-Assembly of Cellulose Nanocrystal and Precursor









1. Mesoporous material: silica, carbon, resin, TiO_2 , etc.
2. Monolith: hydrogel, aerogel
3. Optical material: photonic matrix coupled with functional guest particle
4. Ink for soft lithography

Nature **2010**, *468*, 422-425

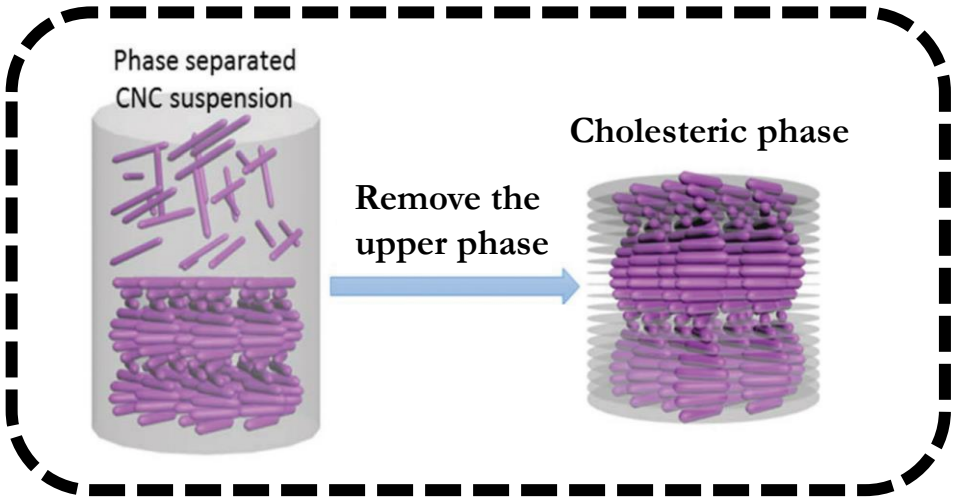
Angew. Chem. **2012**, *124*, 6886-6890

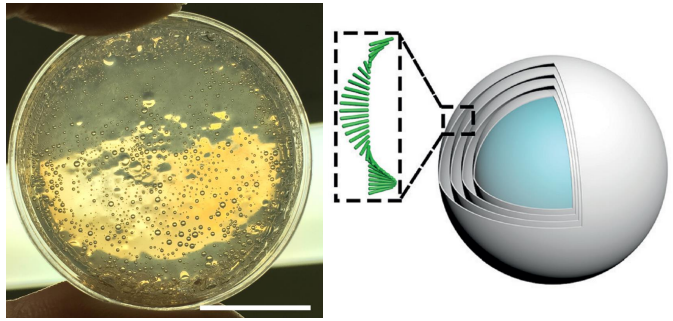
J. Am. Chem. Soc. **2014**, *136*, 4788-4793

Chem. Mater. **2017**, *29*, 3980-3988

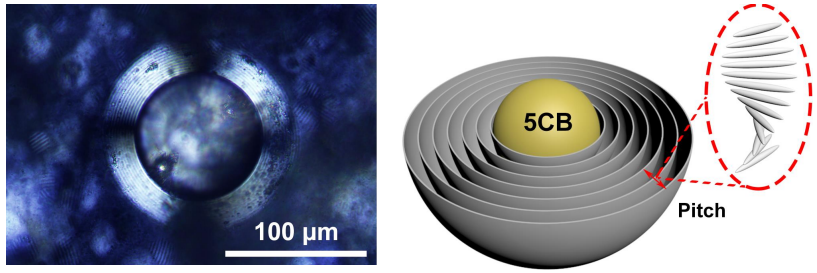
Matter **2019**, *1*, 988-1000

Cellulose Nanocrystal as Liquid Crystal Colloids: Bubbles, Emulsions and Glass

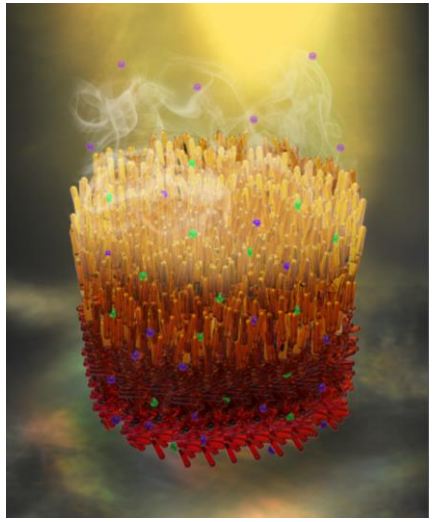




Liquid Crystal Bubble

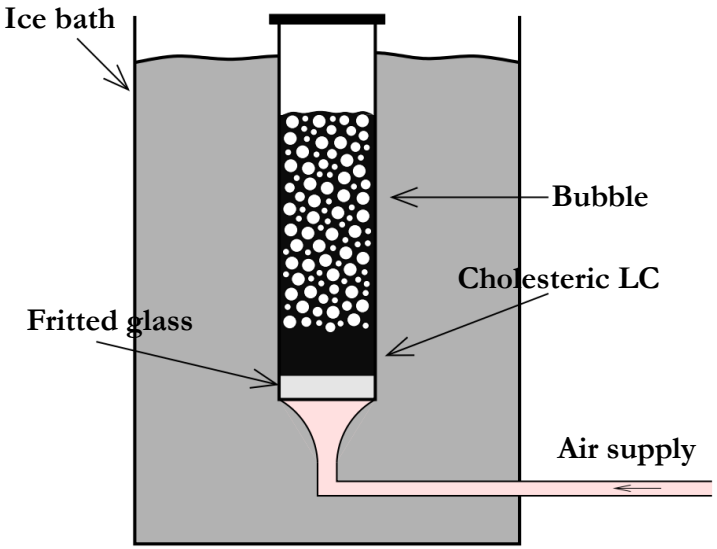


Liquid Crystal-in-Liquid Crystal Emulsion

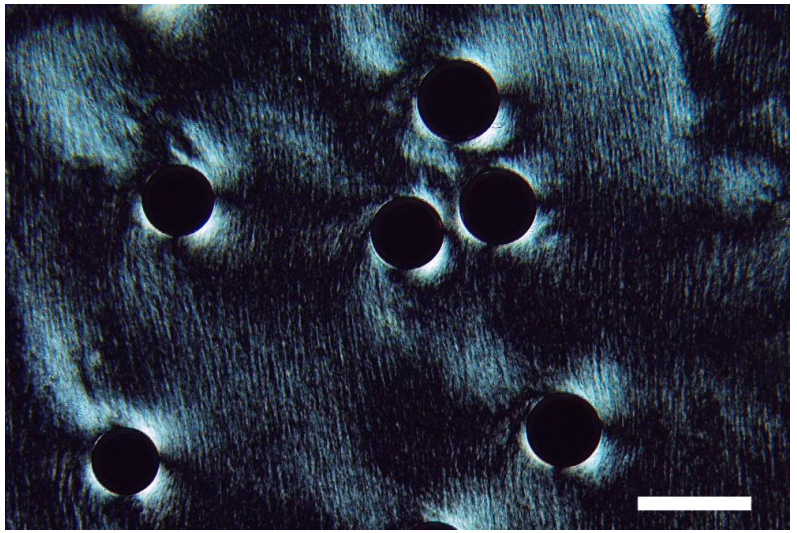


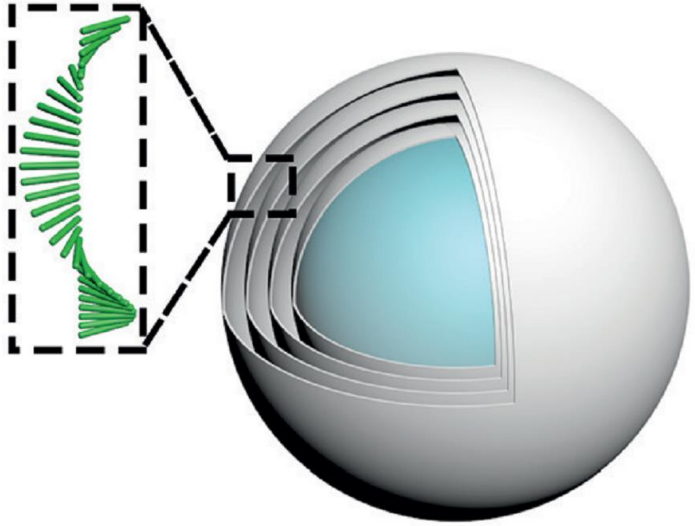
Liquid Crystal Colloidal Glass

G. Chu, Angew. Chem. **2017**, *129*, 8877-8881
G. Chu, Langmuir **2018**, *34*, 13263-13273
G. Chu, ACS Nano **2020**, *14*, 13380-13390
G. Chu, Langmuir **2020**, *36*, 979-985

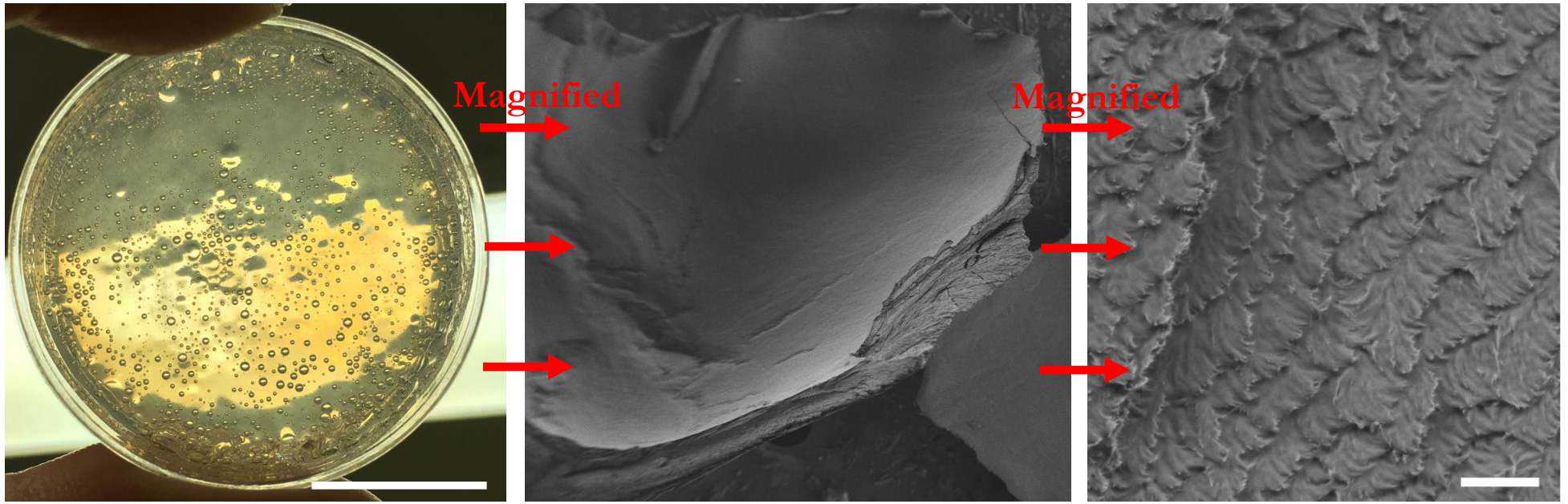


Bubble generation setup



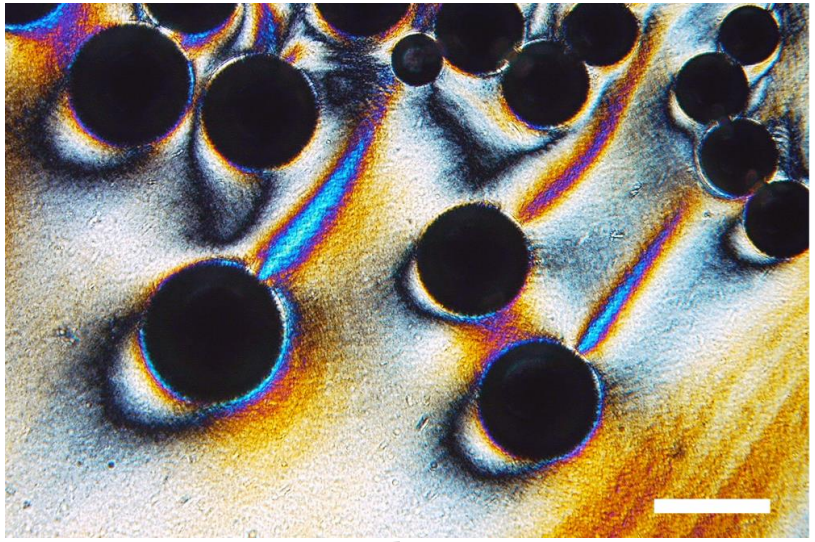


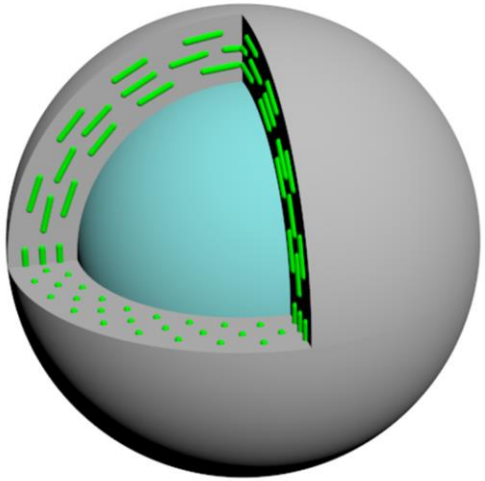
Cholesteric ordered bubble

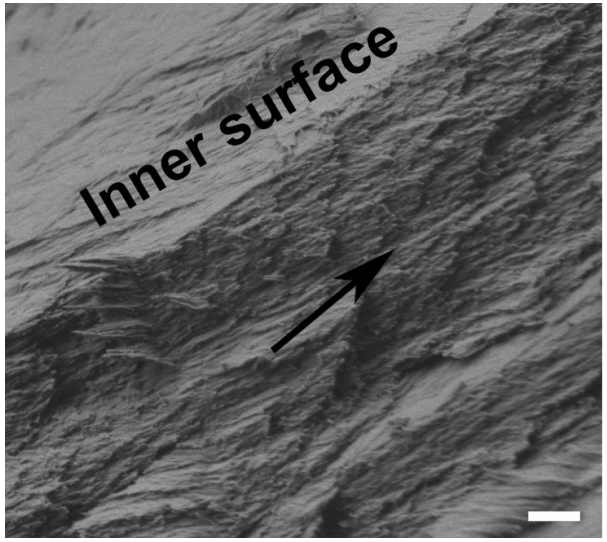


Solidification of cholesteric bubble in hydrogel

G. Chu, Angew. Chem. **2017**, *129*, 8877-8881







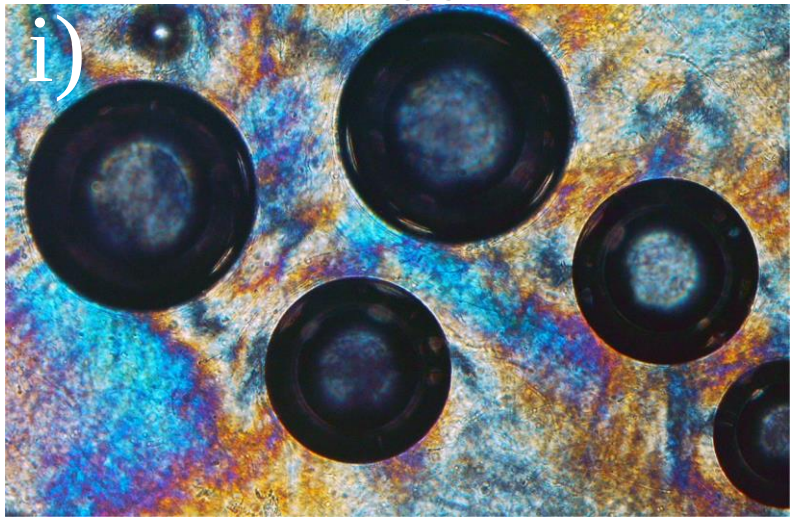
Structure, texture and generation of nematic ordered cellulose bubble

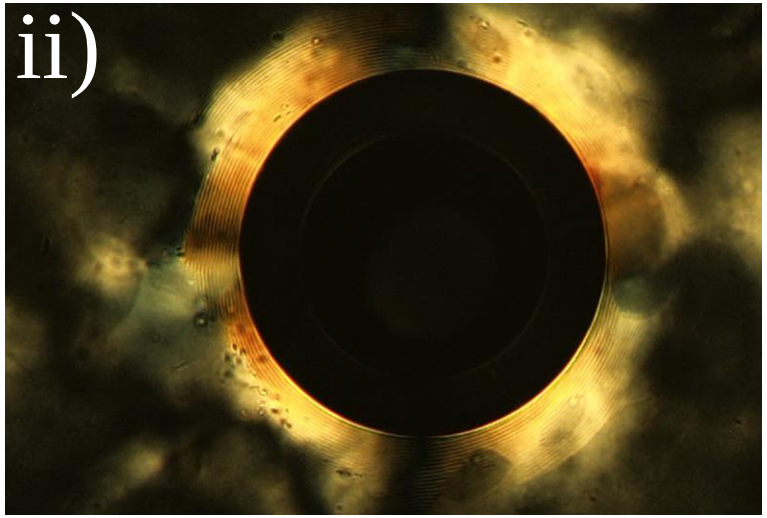
Nematic ordered bubble

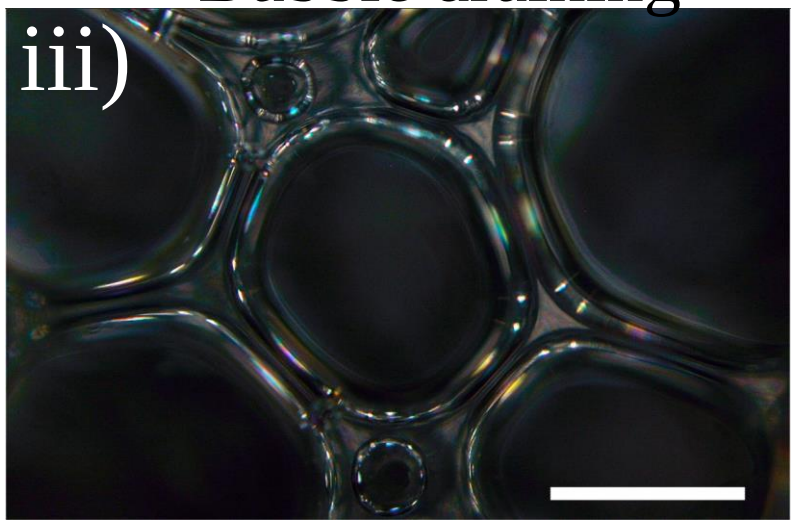
Initial

Cholesteric

Bubble draining

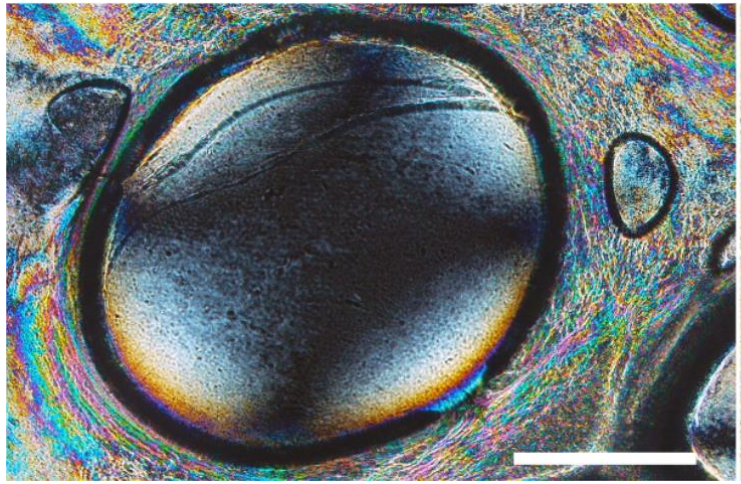




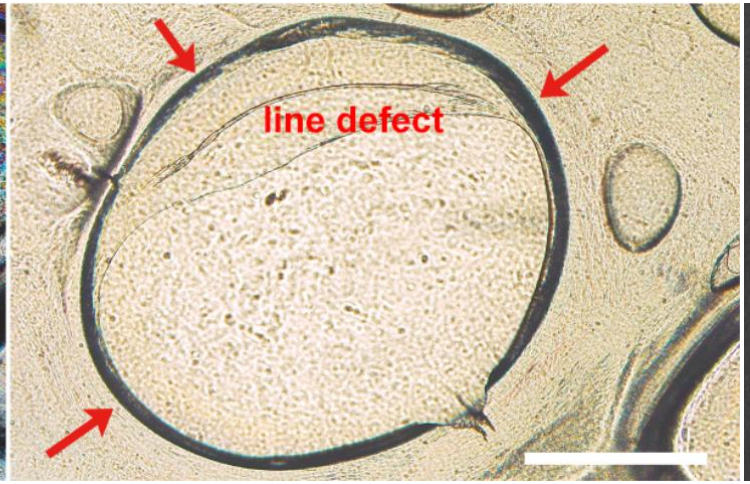


Evaporation

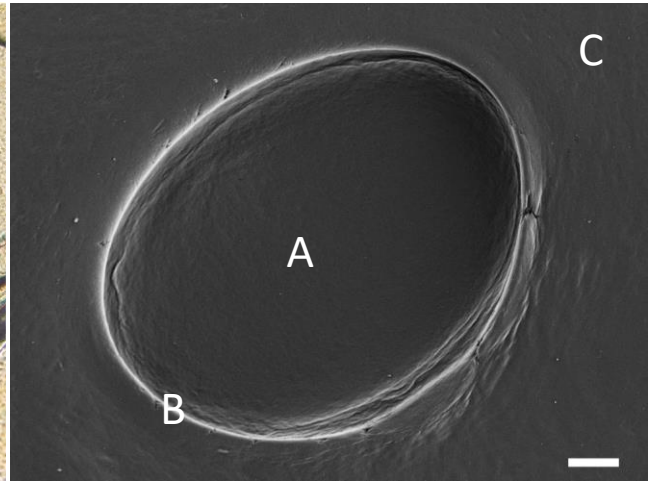
G. Chu, Angew. Chem. **2017**, *129*, 8877-8881



Crossed-polarized



Depolarized



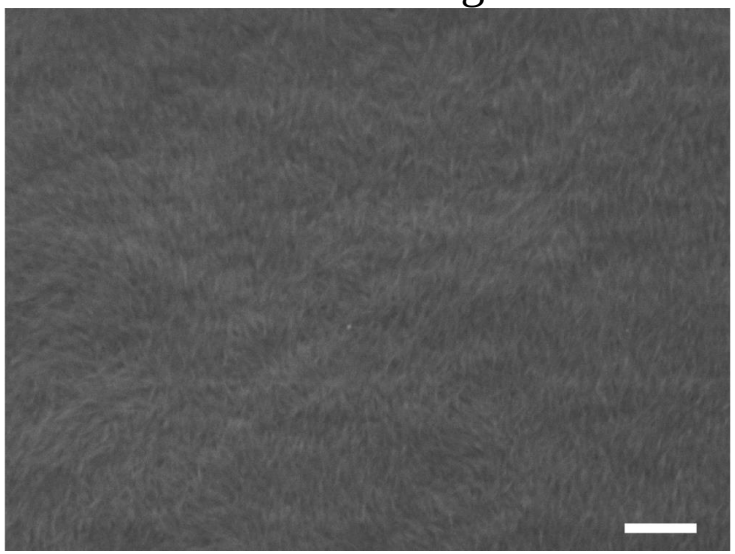
SEM

Optical images of the dry bubble films

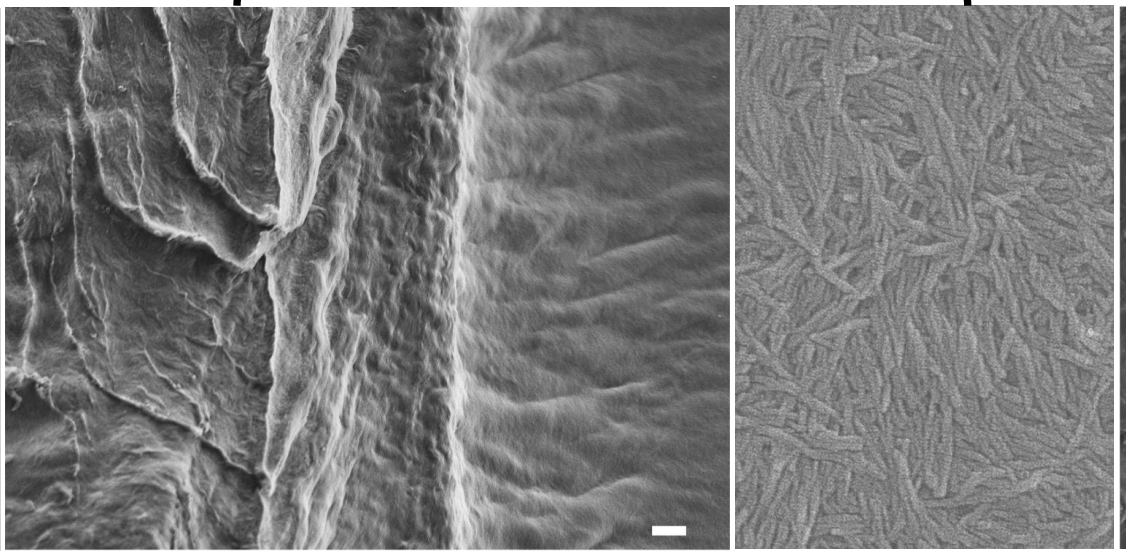
A: Bubble region

B: Boundary region

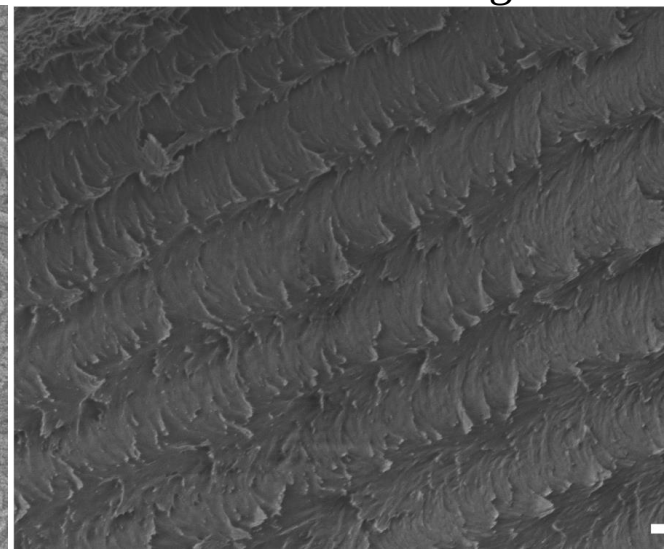
C: Bubble free region



Nematic arrangement



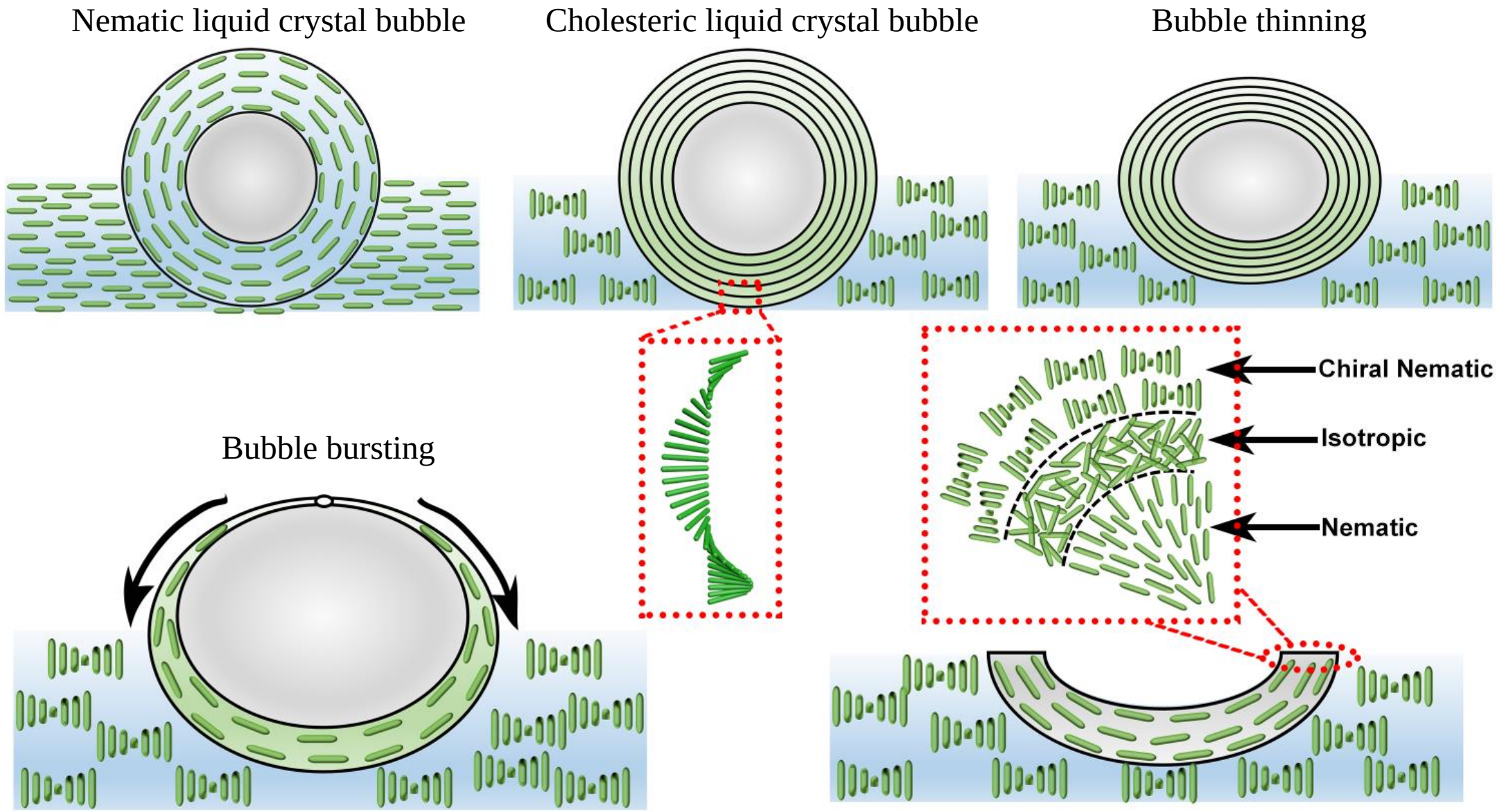
Isotropic arrangement



Cholesteric arrangement

G. Chu, Angew. Chem. **2017**, *129*, 8877-8881

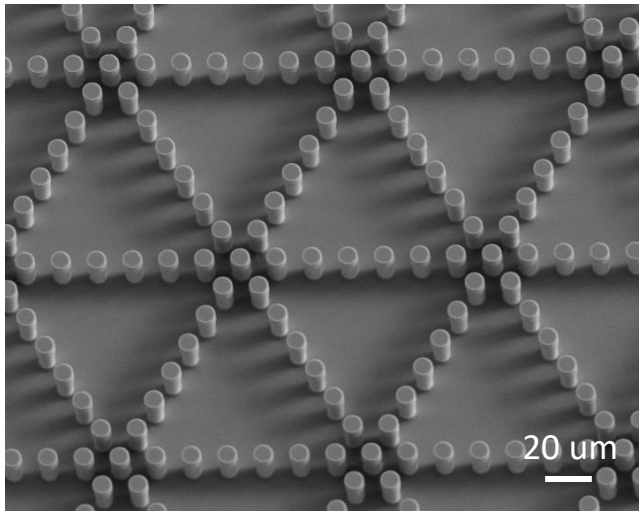
Structural Transition in Liquid Crystal Bubbles during Evaporation



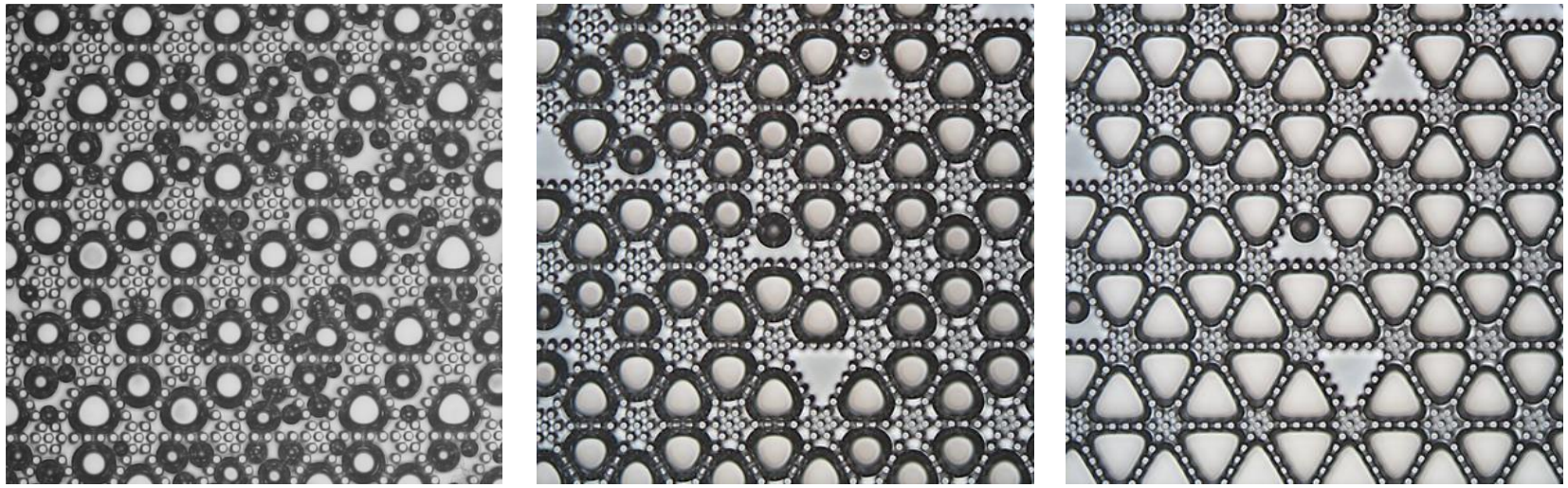
G. Chu, *Angew. Chem.* **2017**, *129*, 8877-8881

2D Confined Liquid Crystal Bubbles

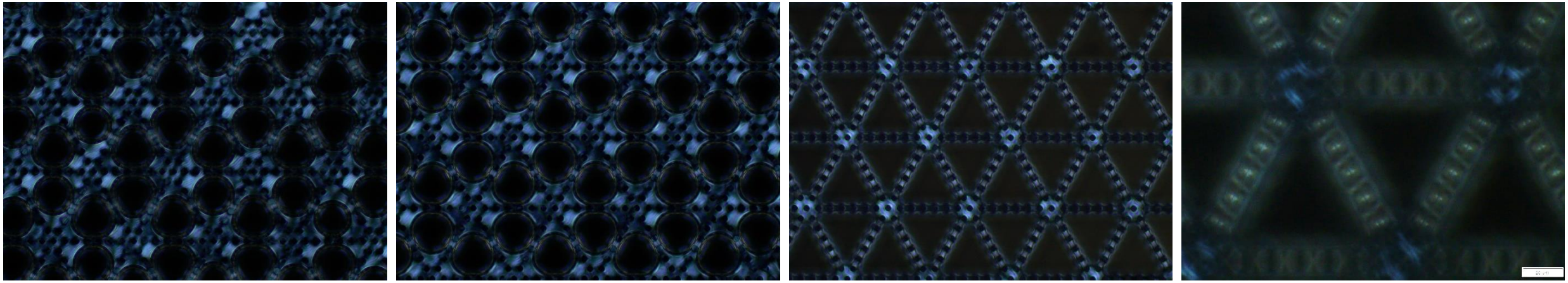
Pillar-structured silicon substrate



t = 0 h →



Liquid Crystal Bubble Draining in 2D Confined Space

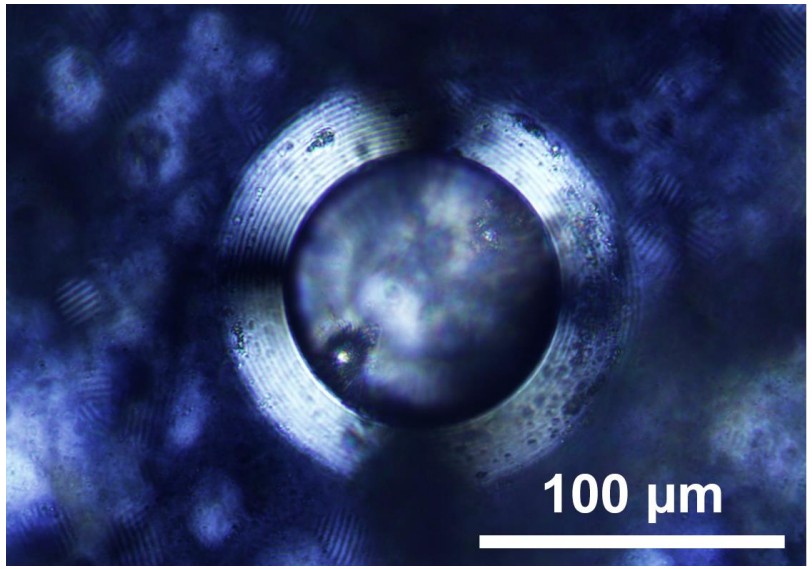


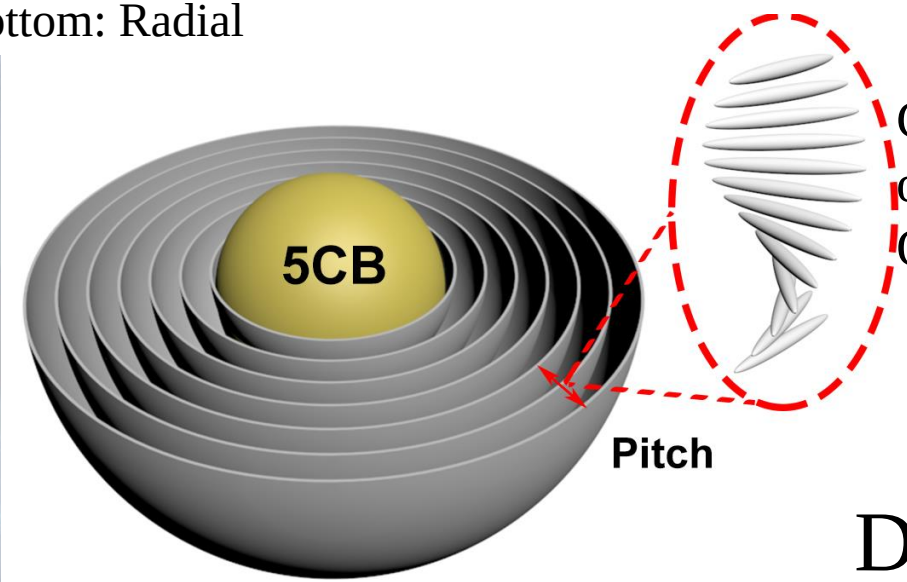
t = 0 h →

G. Chu, In preparation

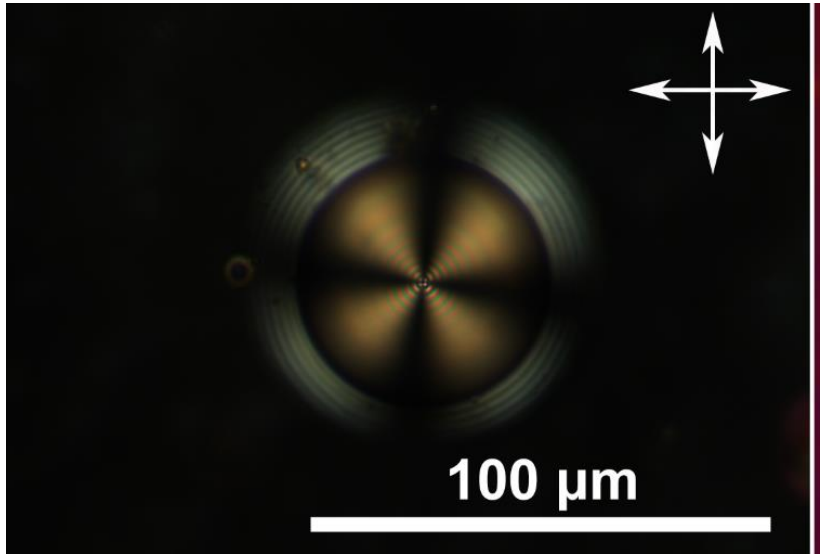
Liquid Crystal-in-Liquid Crystal Emulsion: Hard Colloids in Liquid Crystal

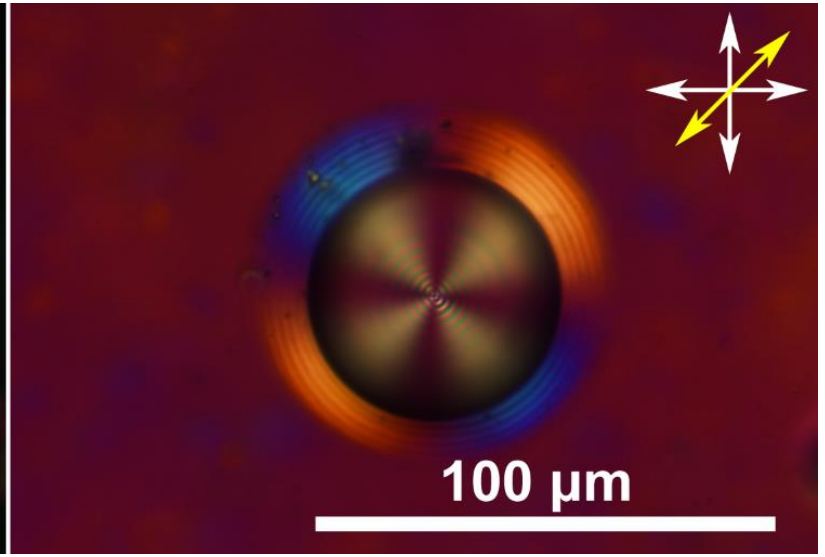
Nematic-in-Cholesteric liquid crystal Emulsion
Upper: Bipolar Bottom: Radial





Continuous Phase: Cholesteric ordered cellulose nanocrystal
Oil Phase: Nematic 5CB liquid crystal





Diameter-to-Pitch Ratio

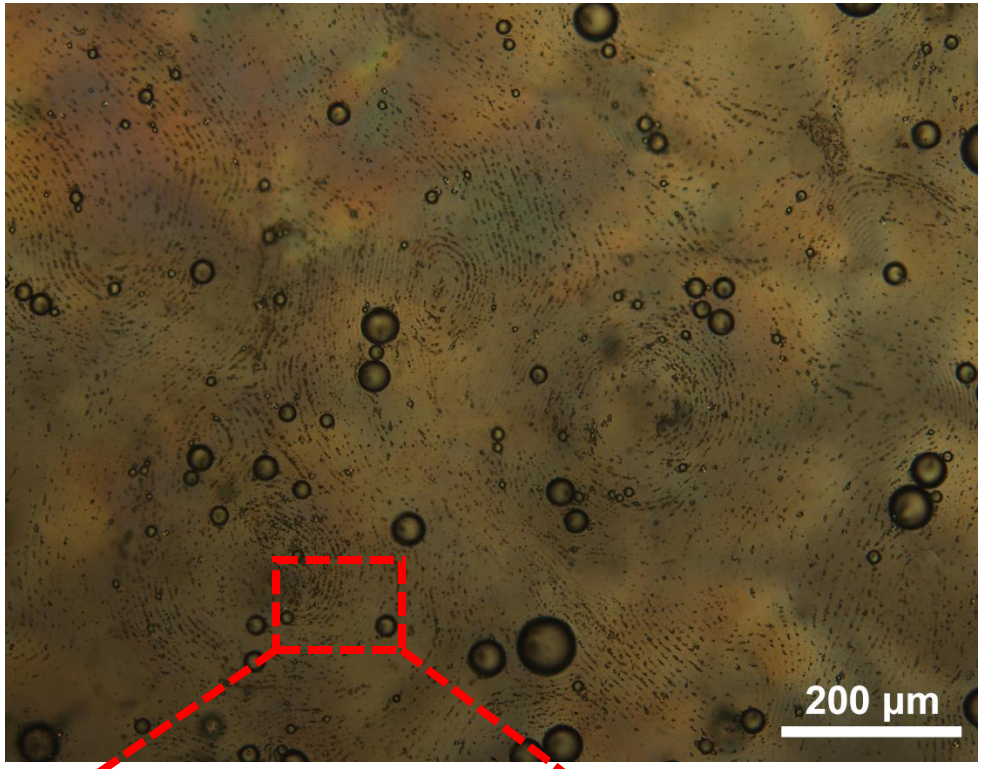
$$\alpha = D/p$$

$\alpha >> 1$ Strongly twisted emulsion

$10 \leq \alpha \leq 30$

Core-shell structured emulsion

G. Chu, Langmuir **2018**, *34*, 13263-13273



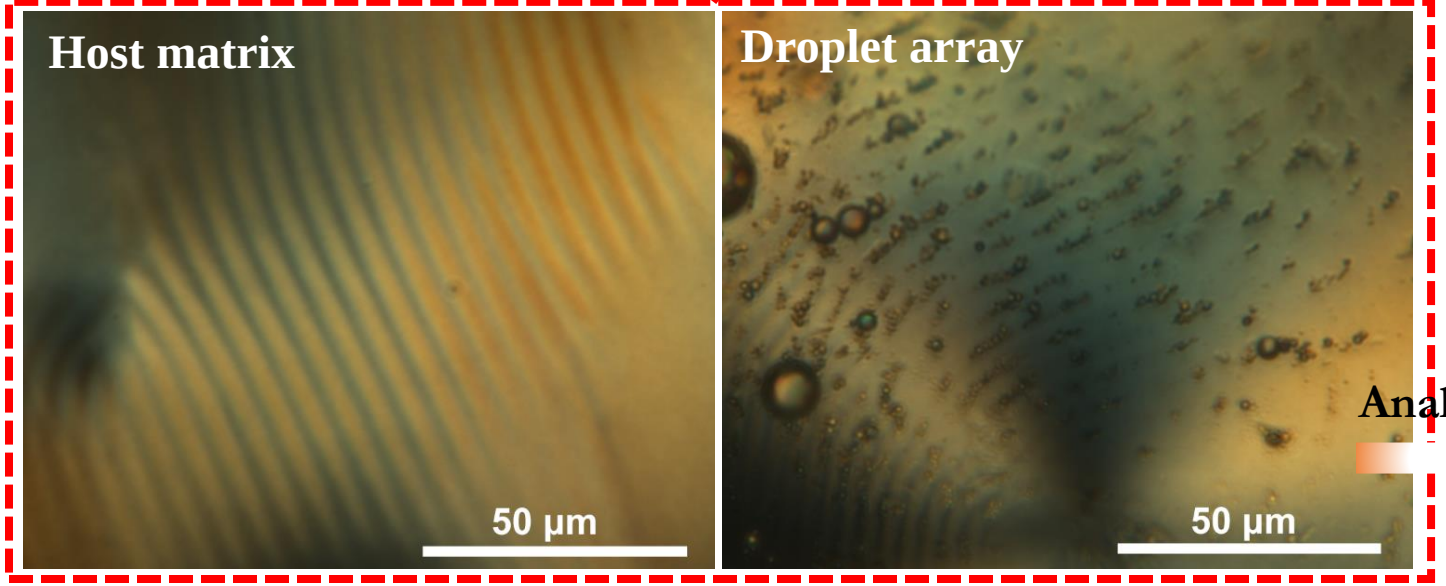
Diameter: Decrease
Pitch: Increase

Long-range structuring of emulsion droplets by mimicry of fingerprint texture

$\alpha<1$ Weakly twisted emulsion

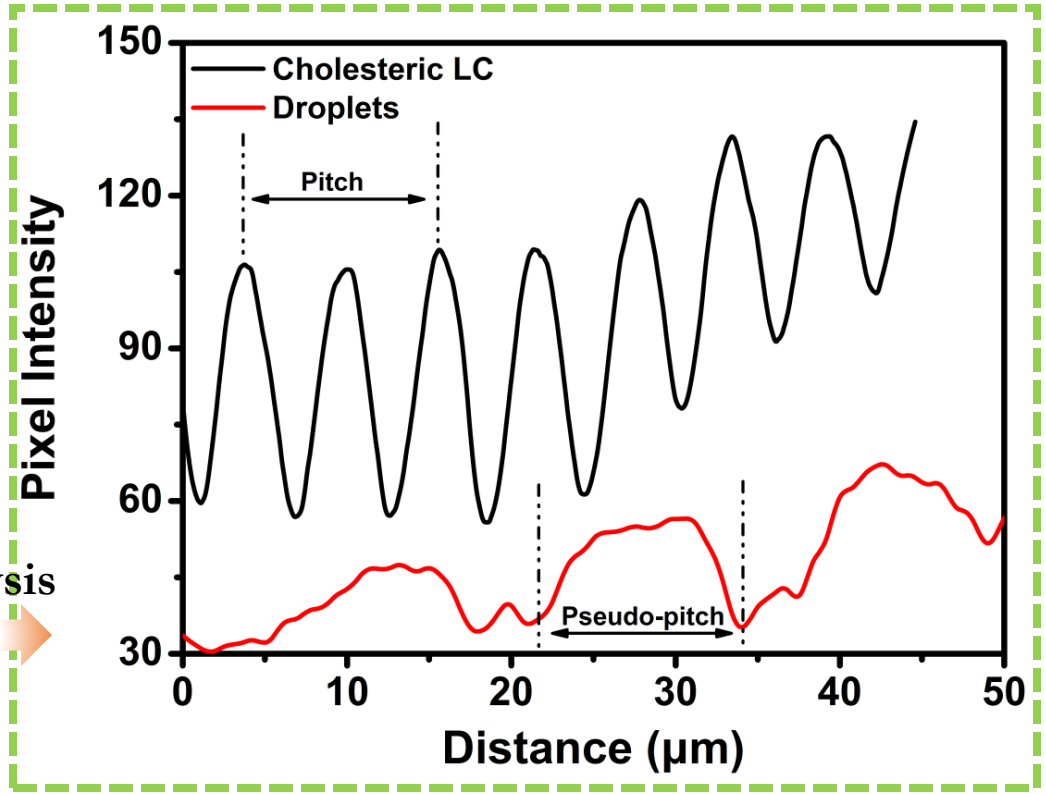
$\alpha = 1/6$

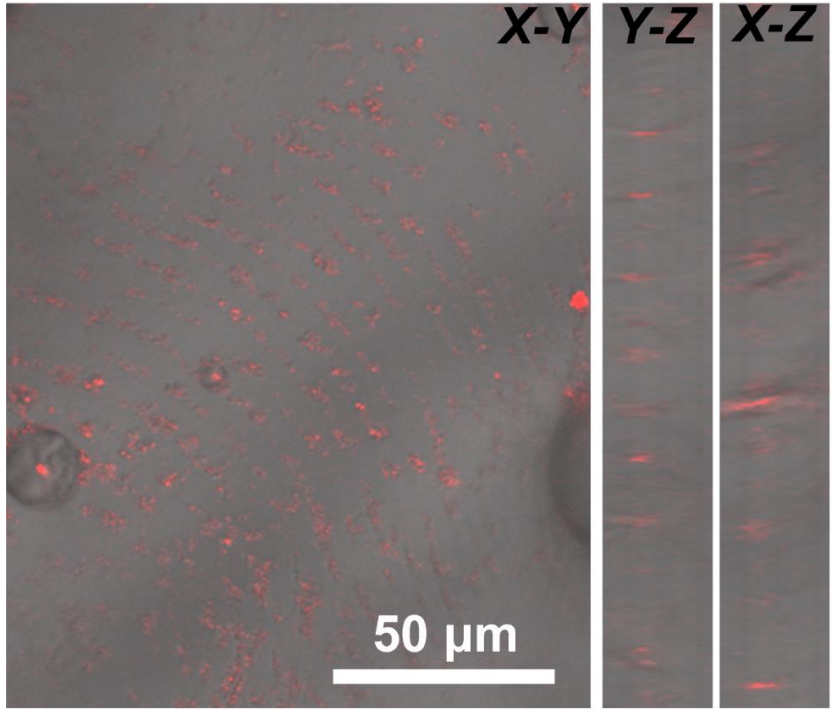
Fingerprint droplets array in chiral nematic host matrix



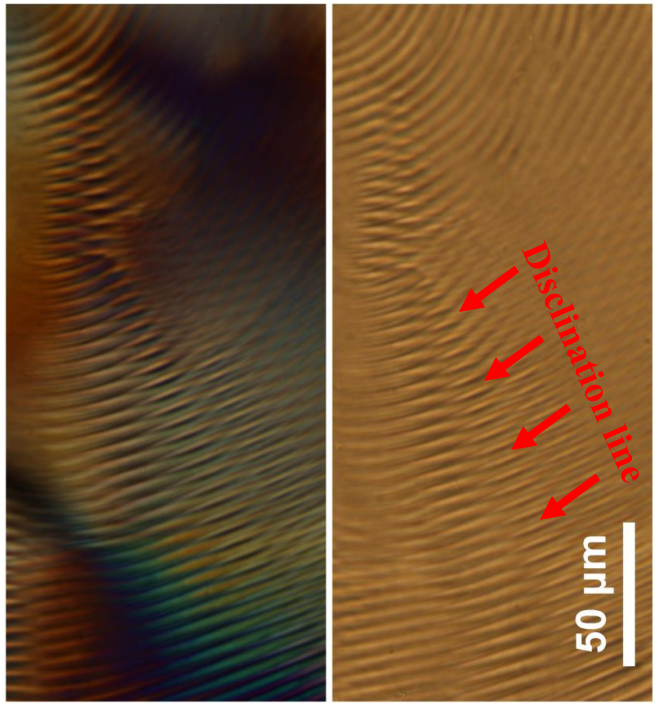
Analysis

Pitch: 12.0 μm Pseudo-pitch: 12.2 μm

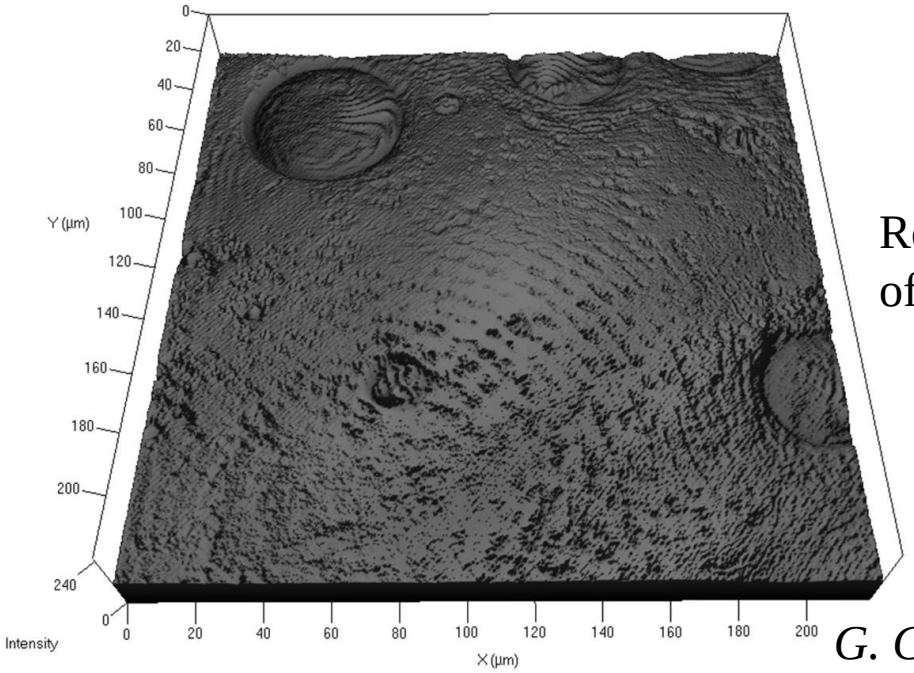




Polarized confocal laser scanning microscopy of the droplet array

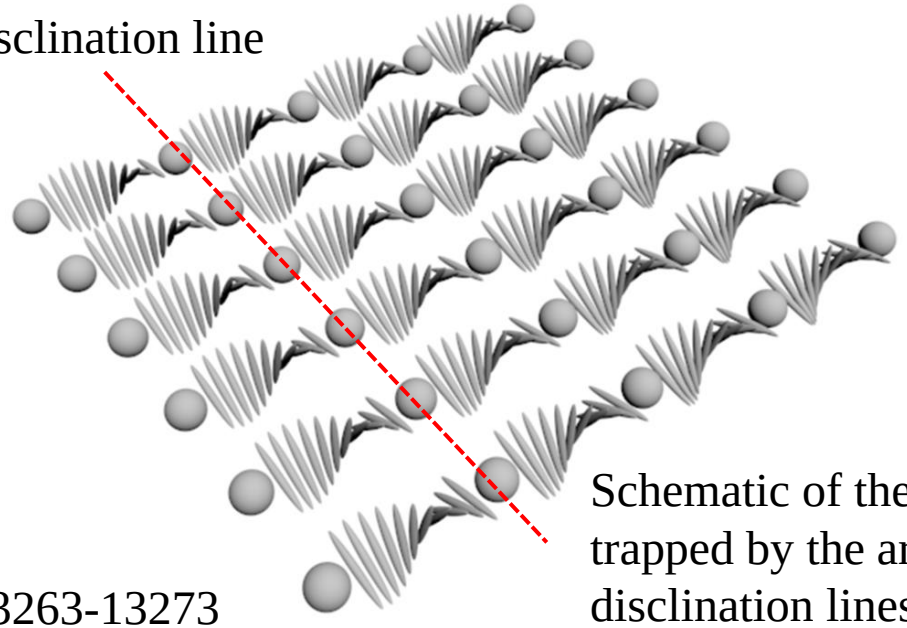


Polarized (left) and bright field (right) images with long-range disclination line in chiral nematic matrix



Reconstructed 3D structure of the droplet array

Disclination line

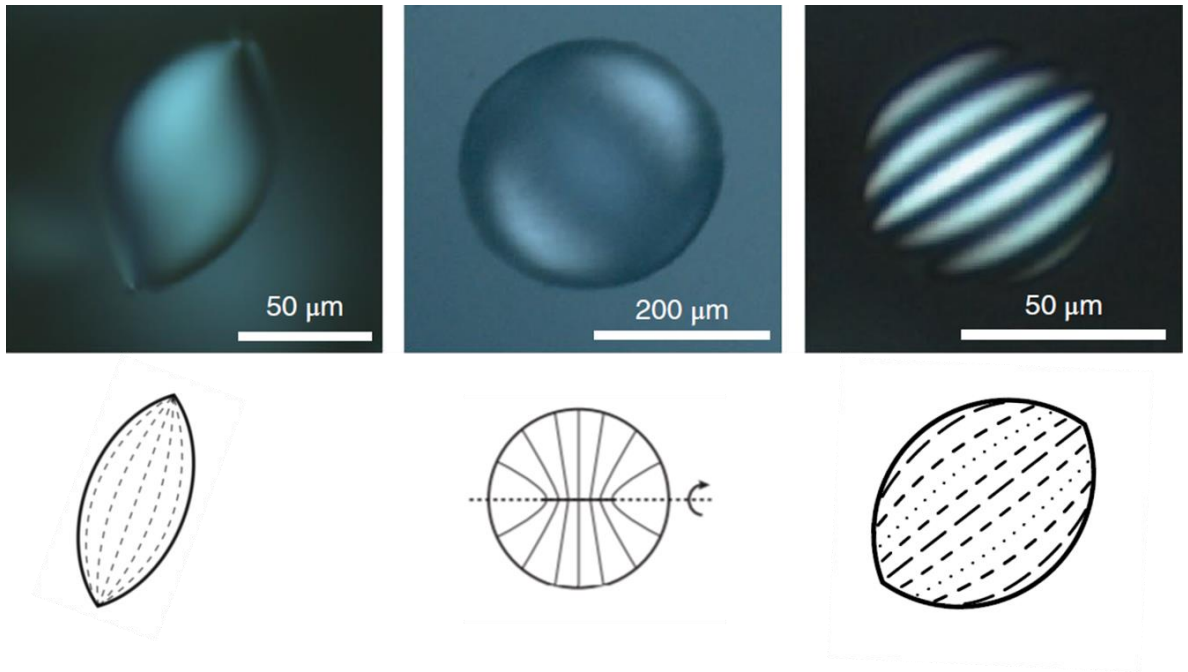


Schematic of the droplets trapped by the array of disclination lines

G. Chu, *Langmuir* **2018**, *34*, 13263-13273

All-Aqueous Liquid Crystal Emulsion: Soft Colloids in Liquid Crystal

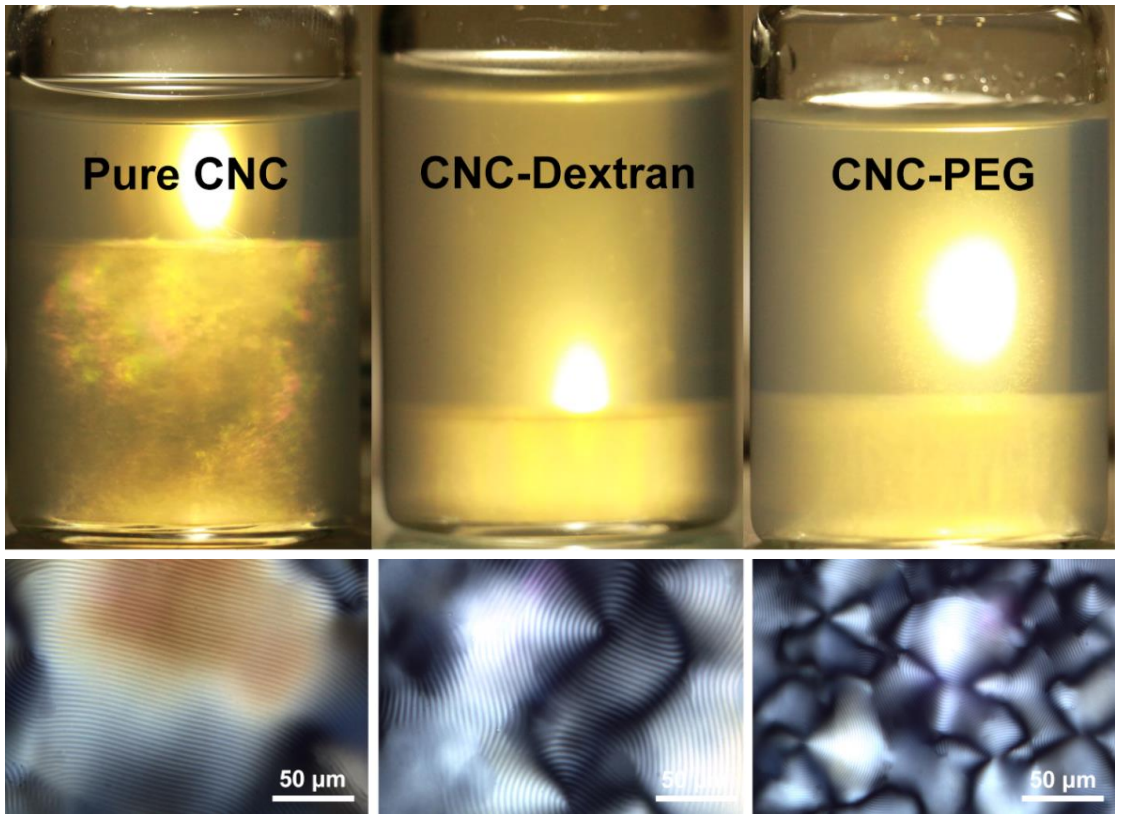
Tactoid: Anisotropic droplet suspended in isotropic continuous phase



Spindle **Spherical** **Uniaxial**

Merge; Unstable; Phase Separation

Adding **Polymer** into CNC liquid crystal



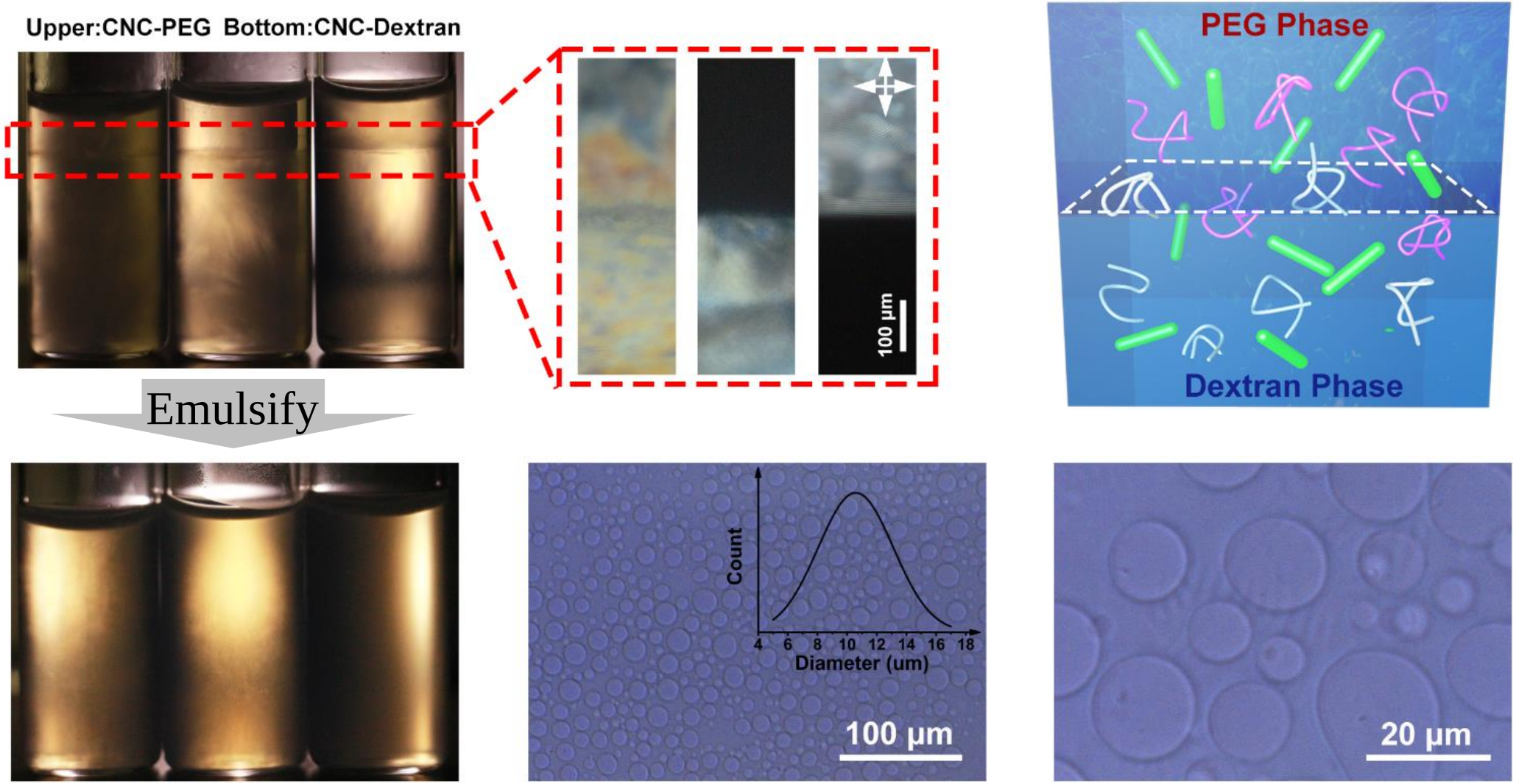
G. Chu, ACS Nano **2020**, *14*, 13380-13390

Mixing immiscible phase: water-in-water emulsion

Macroscopic view

Microscopic view

Nanoscopic view

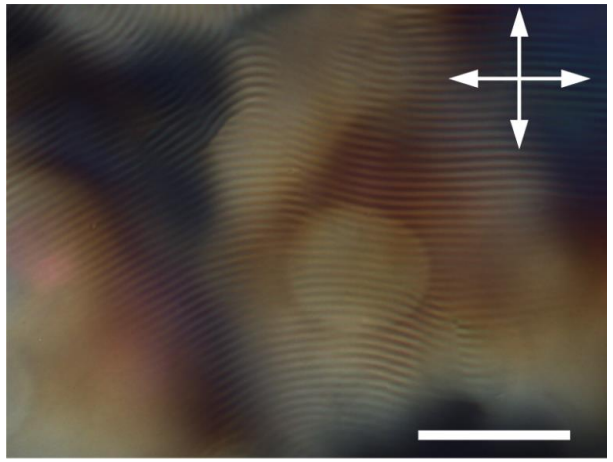


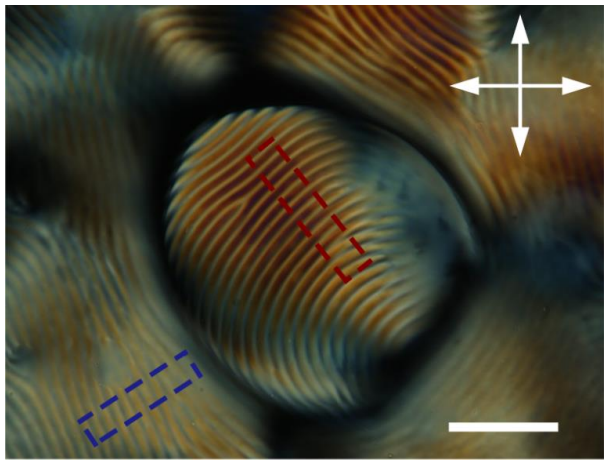
G. Chu, *ACS Nano* **2020**, *14*, 13380-13390

After equilibrium, all-aqueous liquid crystal emulsion was formed

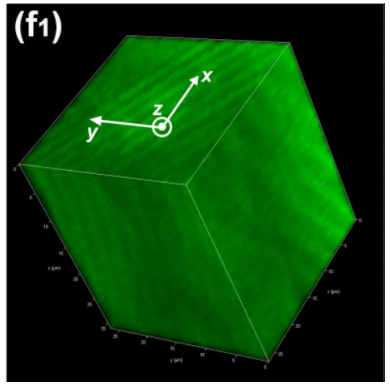
Liquid crystal emulsion

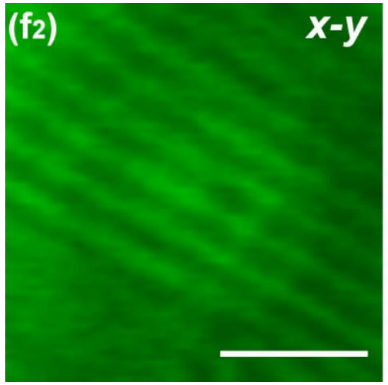
POM image

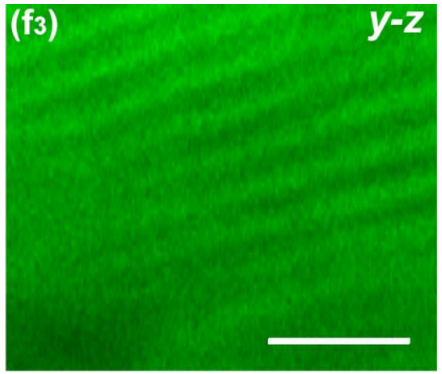


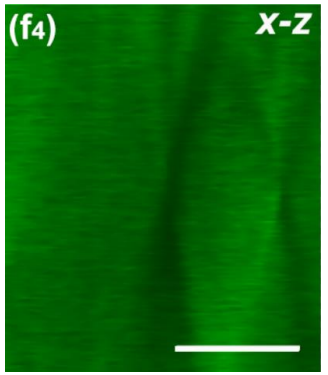


Polarized CLSM



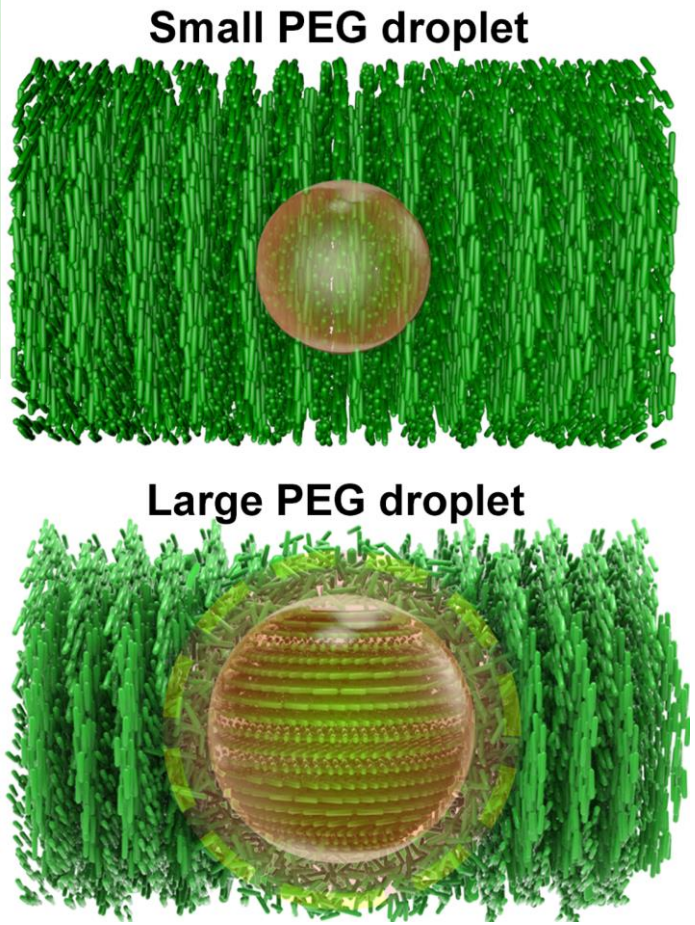






3D reconstruction of cholesteric-in-cholesteric emulsion

Scheme

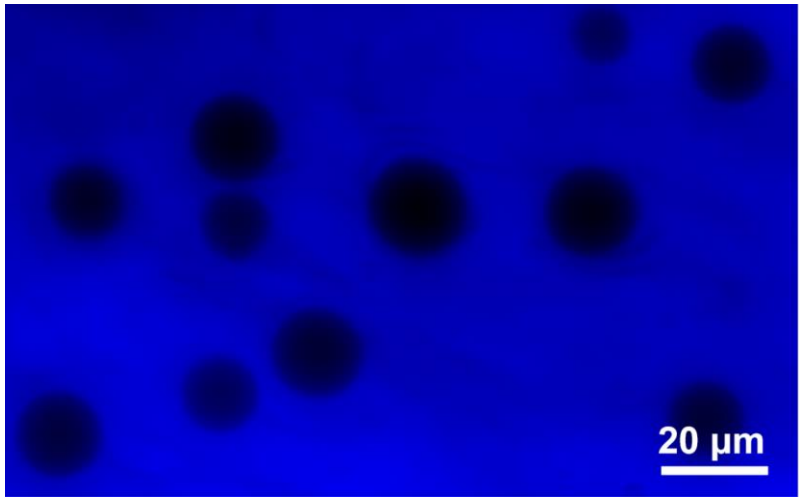


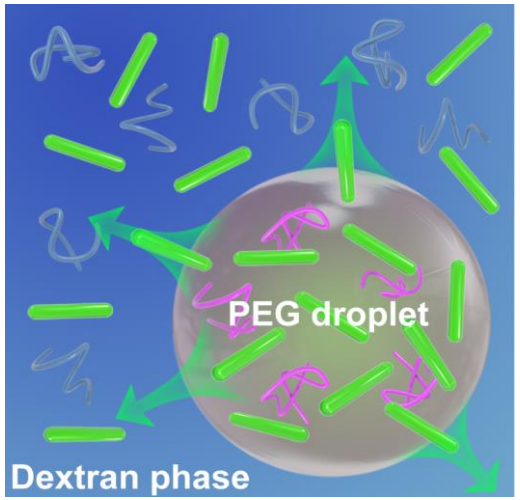
Cholesteric **CNC-PEG droplet** in cholesteric **CNC-Dextran** continuous phase

G. Chu, ACS Nano **2020**, *14*, 13380-13390

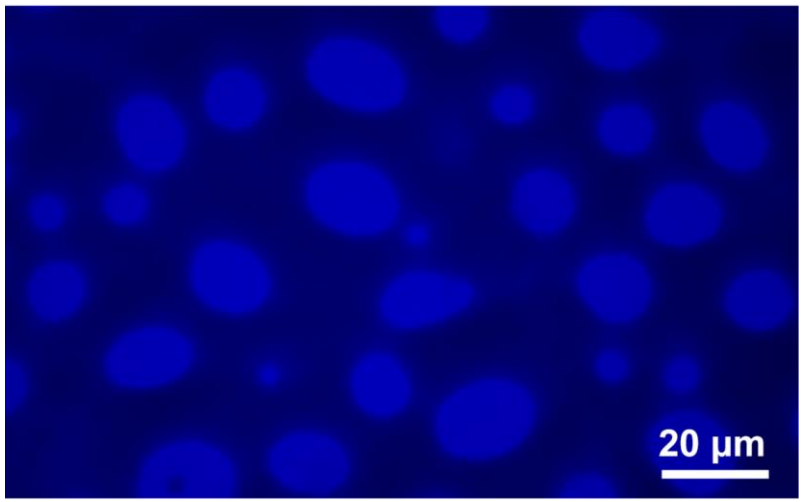
Osmotic driven re-assembly of CNC across the **water-water interface**

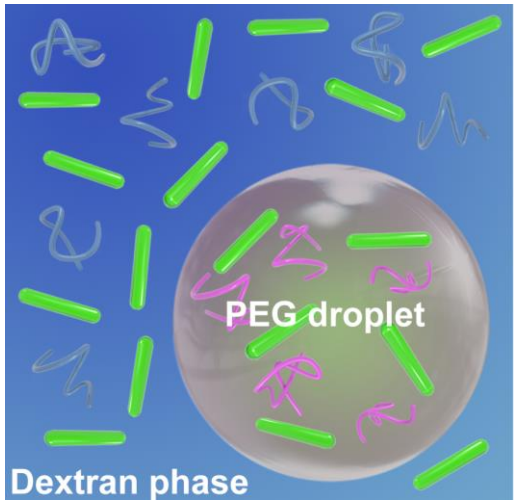
Permeable interactions between continuous phase and suspended droplet





$\Pi_{CNC\text{-}PEG} > \Pi_{CNC\text{-}Dextran}$





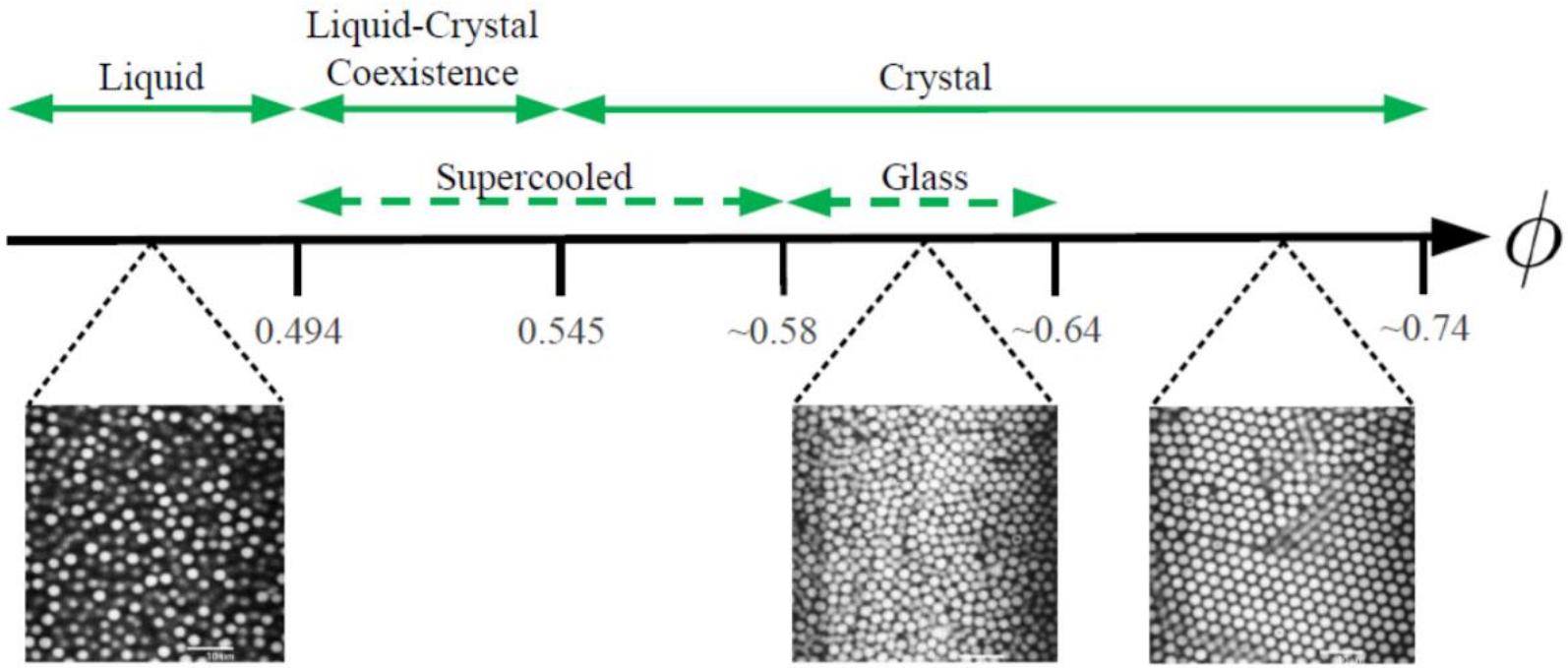
$\Pi_{CNC\text{-}PEG} = \Pi_{CNC\text{-}Dextran}$

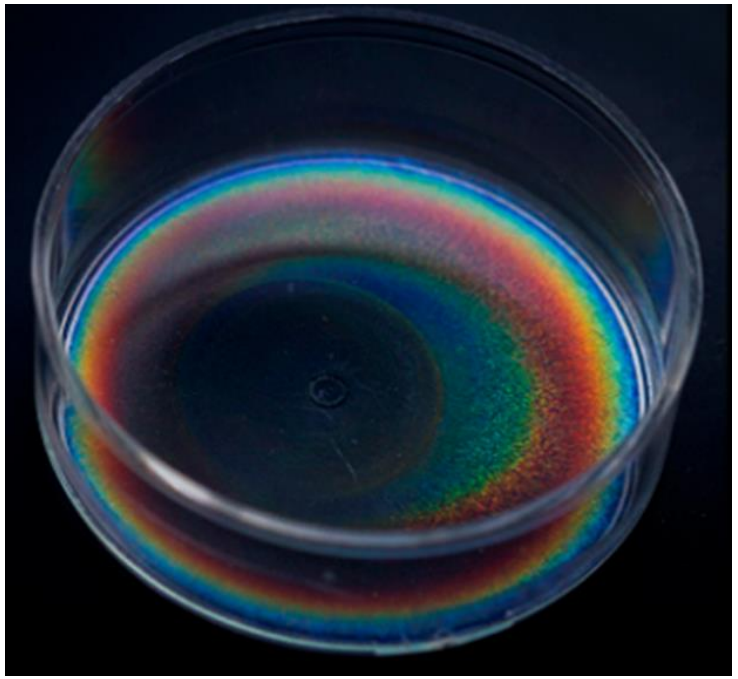
Initial: Dye-labeled CNC **only** in PEG phase

G. Chu, ACS Nano **2020**, *14*, 13380-13390

Nanocellulose Liquid Crystal Colloidal Glass

Simple liquids and complex fluids and soft matter
that depended on volume fraction of colloidal particles.



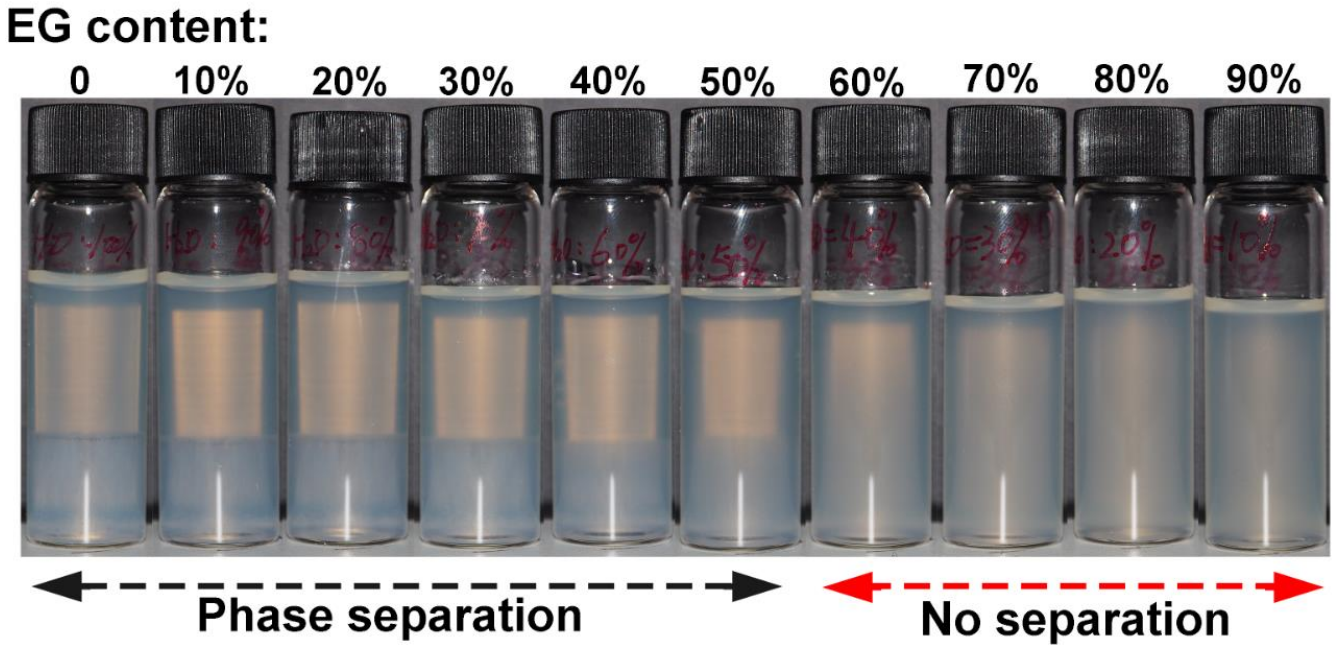


Drying the cellulose suspension exhibits a dramatic **increase in viscosity**. Beyond a certain concentration, the system is said to be a **colloidal glass**.

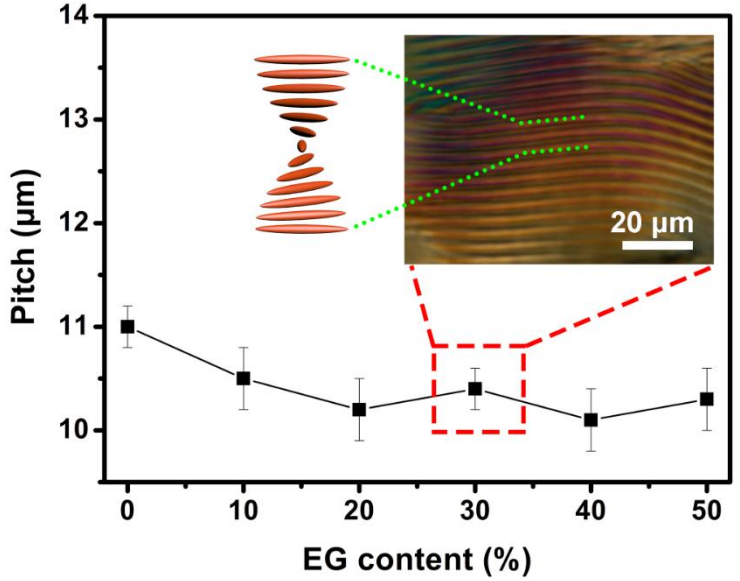
Colloidal glass is solid soft matter that consists of two intertwined phases: a random packed particle network and a fluid solvent, showing solid-like behavior.

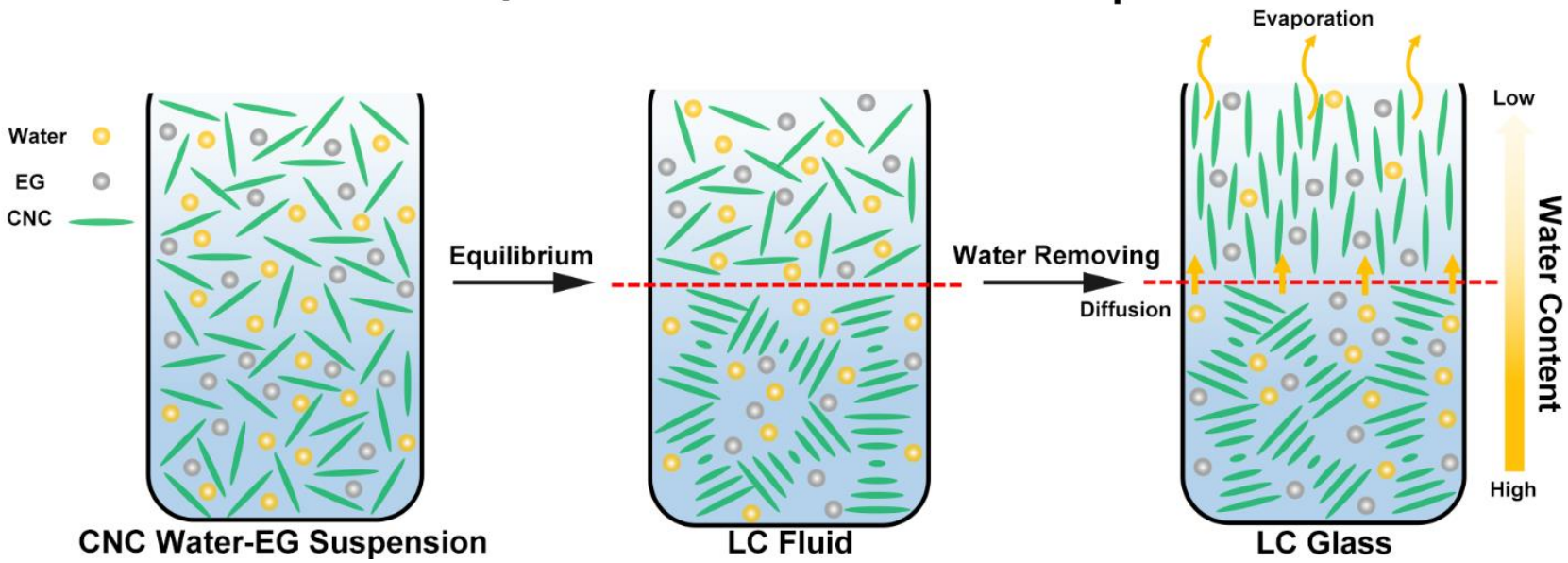
Rep. Prog. Phys. **2012**, *75*, 66501
G. Chu, *Langmuir* **2020**, *36*, 979-985

Cellulose nanocrystal water-ethylene glycol (EG) suspension

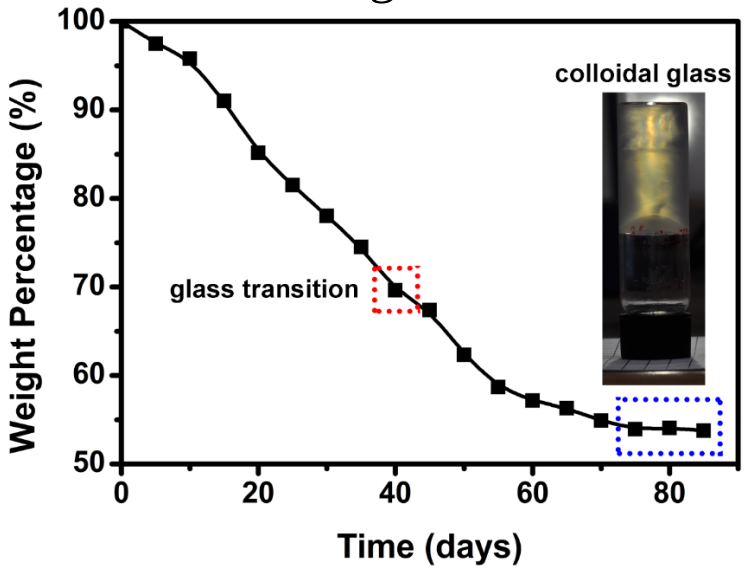


Pitch variation on EG content



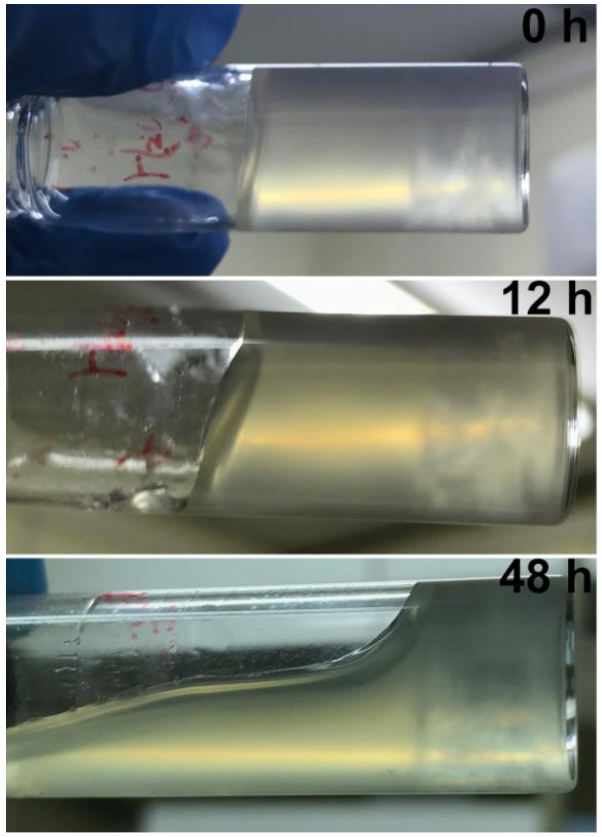


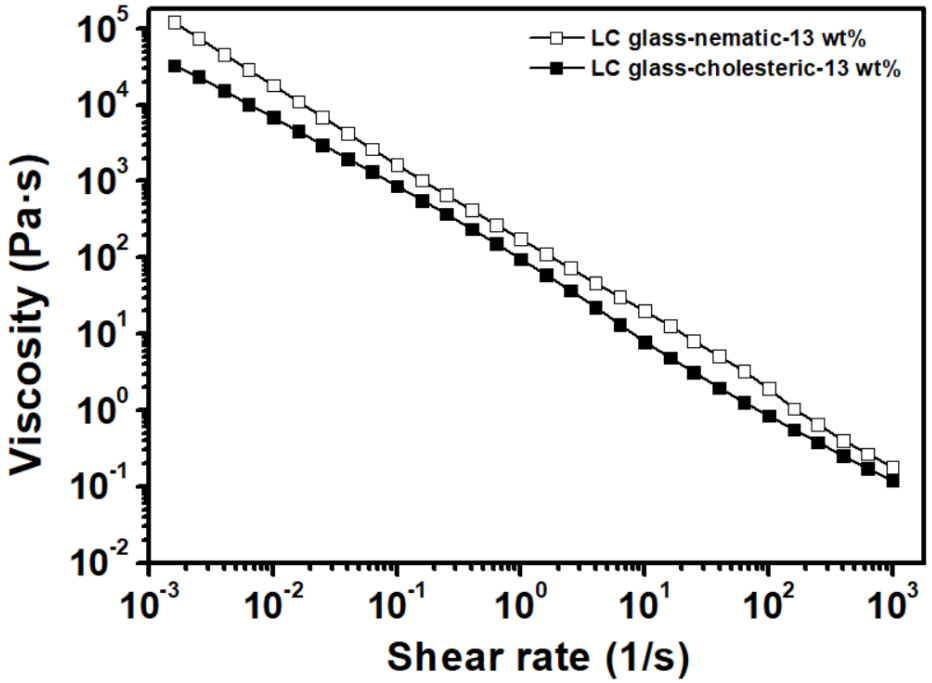
Colloidal glass transition

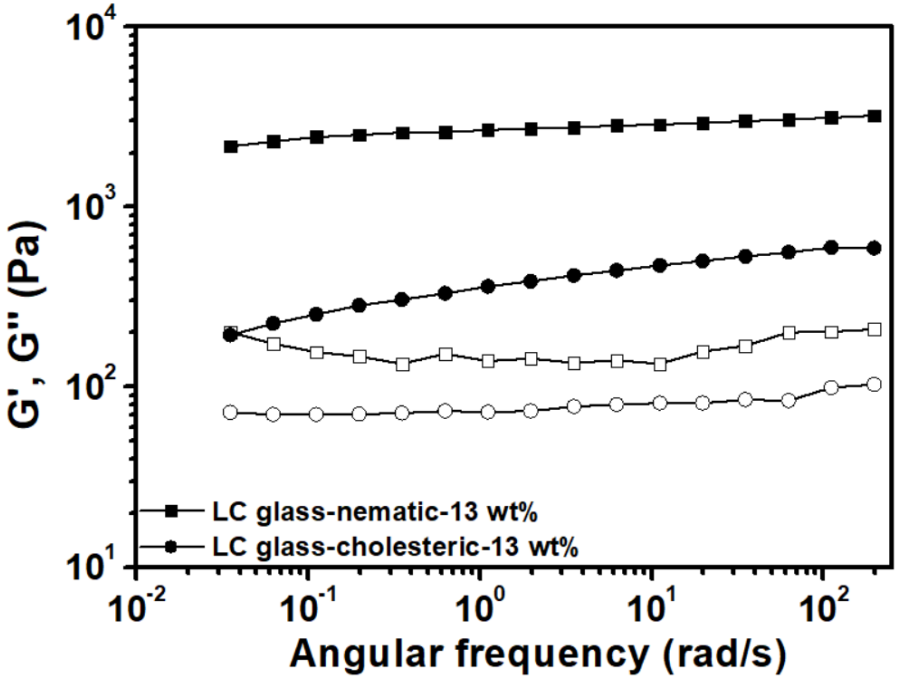


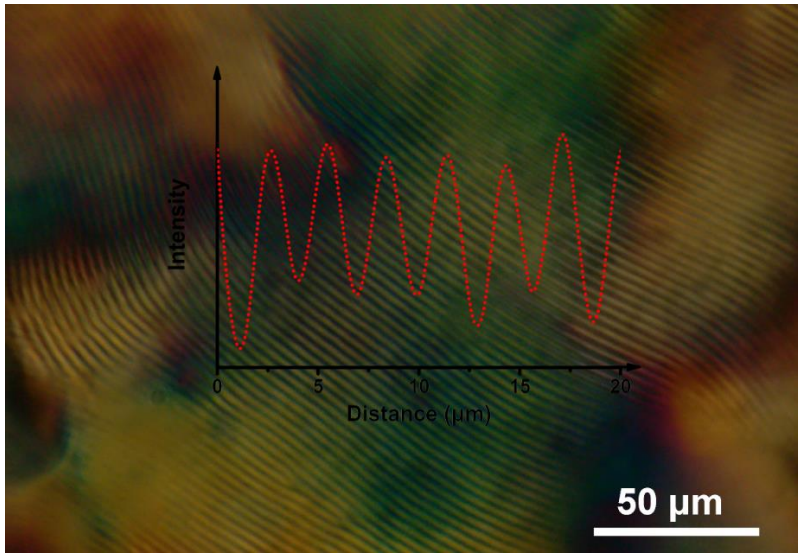
Increase volume fraction of cellulose nanocrystals through selective solvent removing

G. Chu, *Langmuir* **2020**, *36*, 979-985









Nanocellulose colloidal glass, structurally, the system resembles a liquid, yet motions within the suspension are slow enough that it can be considered essentially frozen.

Structural arrest and phase transition occur simultaneously at high particle concentrations, yielding solid-like behavior as well as a frozen liquid crystal texture.

G. Chu, *Langmuir* **2020**, *36*, 979-985

Conclusions

- Liquid crystal (nematic and cholesteric) bubbles have been prepared by bubbling cellulose nanocrystal suspension, exhibiting ordering transition during the drying process.
- Liquid crystal-in-liquid crystal emulsion (nematic 5CB dispersed in cholesteric cellulose nanocrystal suspension) has been observed, showing ordered hierarchical organization.
- All-aqueous cellulose nanocrystal emulsion with permeable water-water interface was observed, showing osmotic-driven particle self-assembly with global cholesteric organization.
- Long-range ordered cholesteric colloidal glass have been observed through selective solvent removal, displaying solid-like behavior at high particle volume fraction.

Acknowledgement

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Thanks for your attention!

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