Surfactant-Free Oil-in-Water Emulsion Stabilized by Chitin Nanocrystals: A Green Recipe

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Overview

INTRODUCTION	PREPARATION OF NANOCRYSTALS	CHARACTERIZATION	THOUGHT EXPERIMENT
Pickering Emulsion Technology and Chitin Background	TEMPO and PA chitin nanocrystals	Single particle using SAXS and emulsion using microscopy	Using SANS for future experiments

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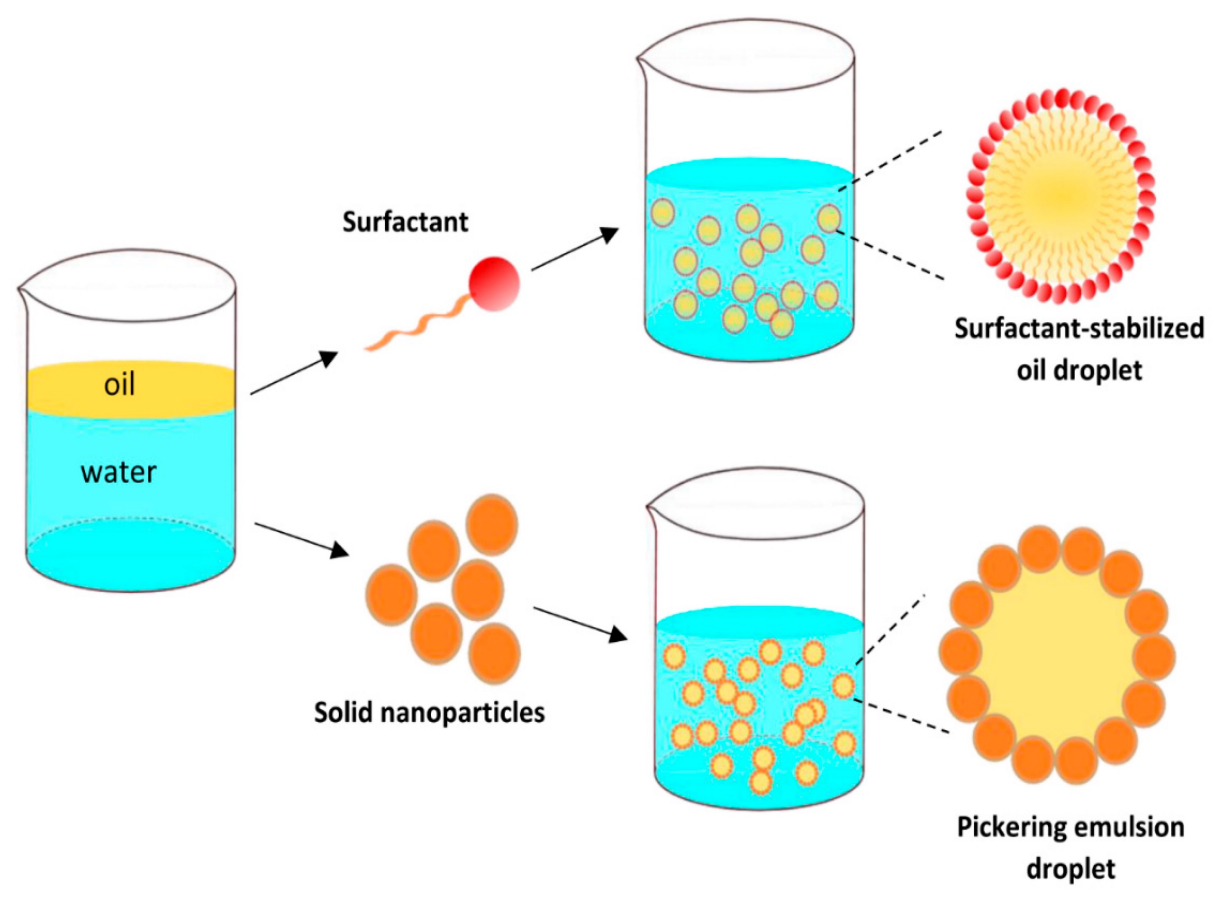
What are Pickering emulsions...



- Conventional emulsions are stabilized by amphiphilic molecular emulsifiers
- Pickering emulsions are **more resistant** to Ostwald ripening and coalescence
- Attributes needed for the particles:
  - Must be **partially wet** by both oil and water phases
  - Lower surface potential
  - Must be **greatly smaller** in scale compared to the target oil droplet size

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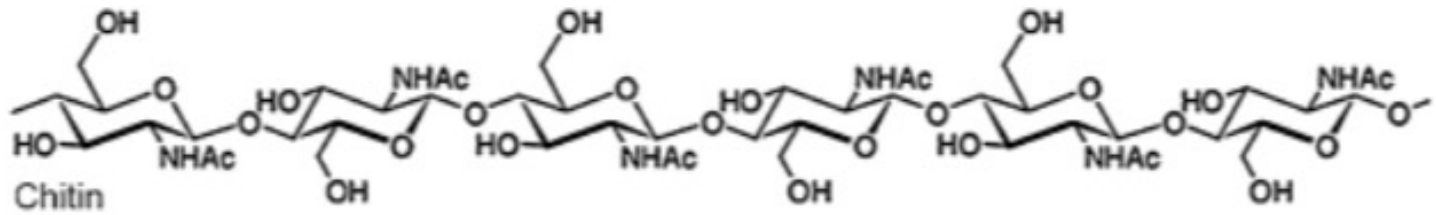
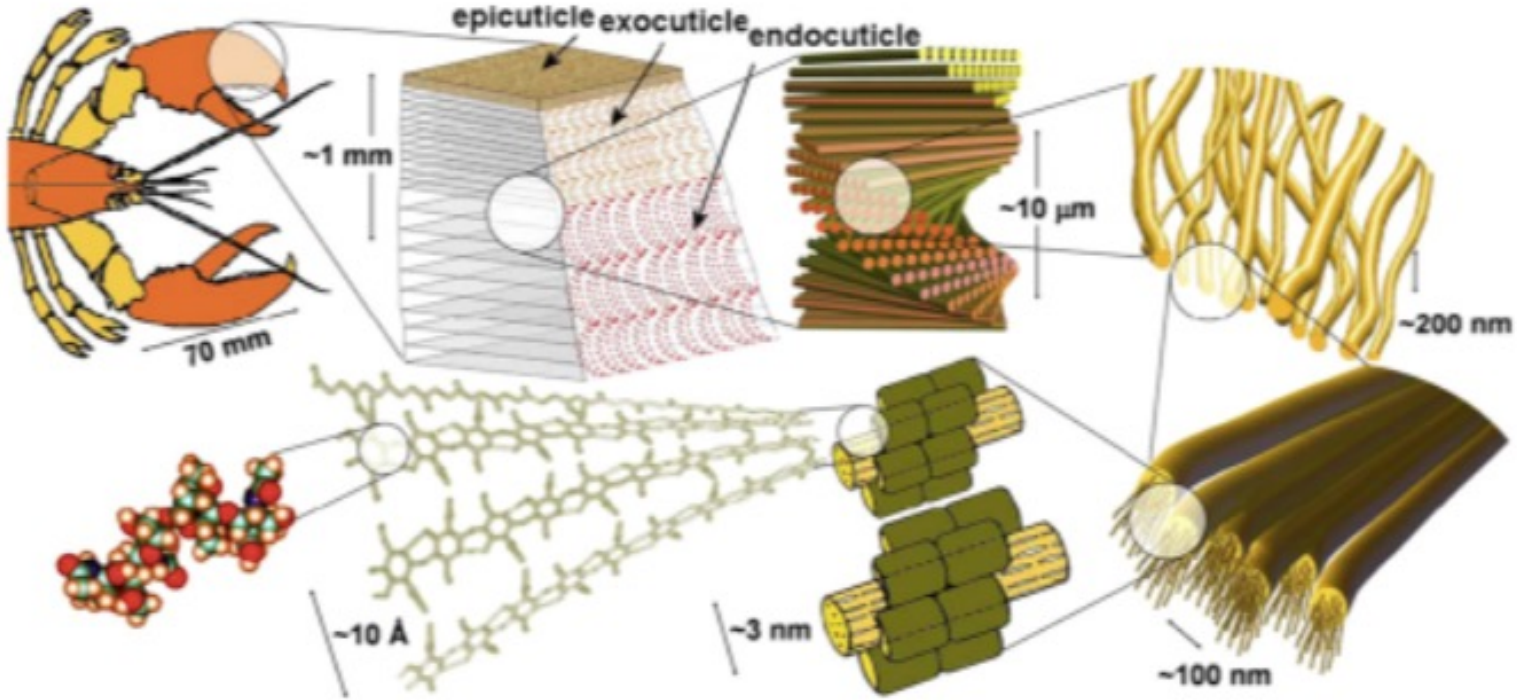
Chitin Background and Research Objective

Objective: To test the chitin nanocrystals and their properties as colloidal particles to an emulsion to provide a green recipe applicable to various food products.

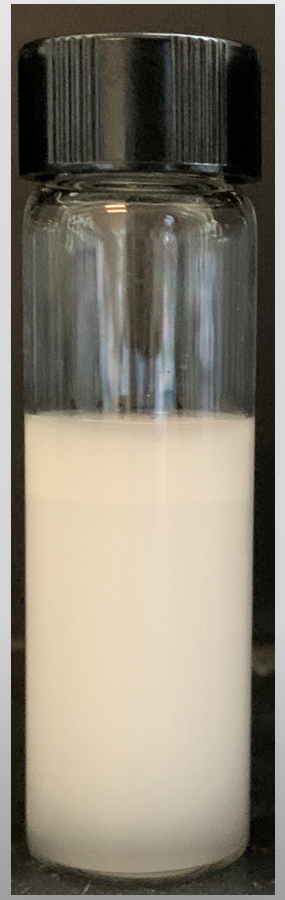
- Second most abundant polymer after cellulose
- In the form of highly **crystalline fibrils** in its biological environment has biocompatibility, and good biodegradability





Task 1: Producing and Analyzing Chitin Nano-whiskers

Preparation of TEMPO oxidized Chitin Nanocrystals



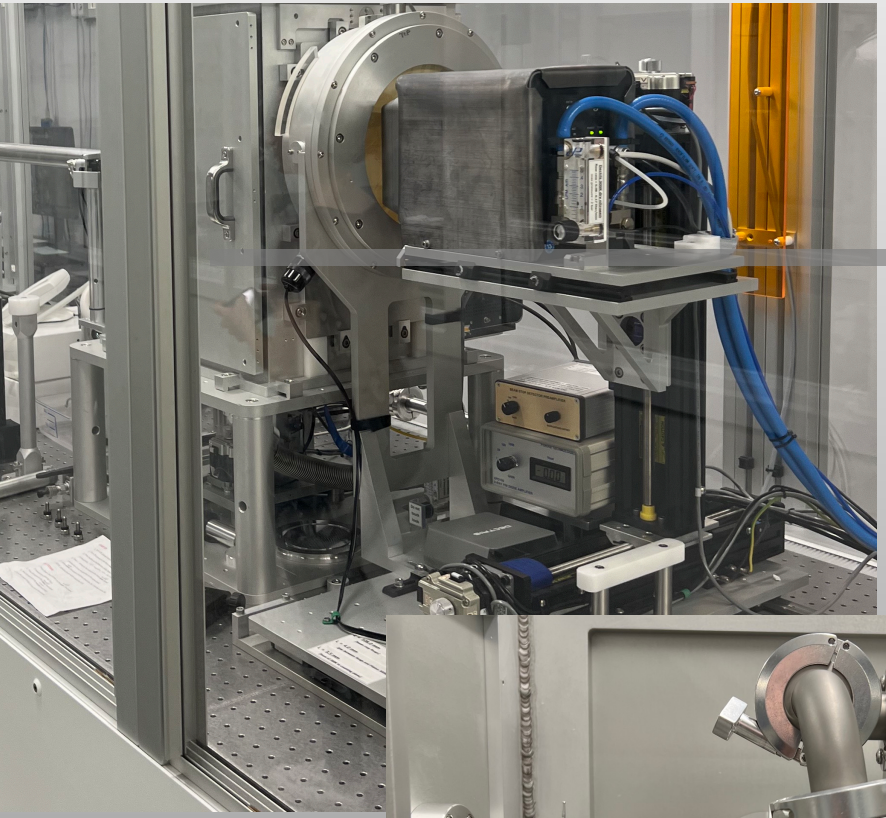
- Preparing Reaction Medium:
  - Chitin + water + TEMPO + NaBr + NaClO
- Alkaline conditions for 2 hours:
  - pH 10.8 at room temperature
- Quenching reaction:
  - adding a small amount of ethanol to the mixture
  - Adjust pH to 7
- Post Processing:
  - Centrifuge 3x at 12000 rpm for 10 min. Remove supernatant by decantation.
- Stored at 4 °C as a permanently wet TEMPO-oxidized chitin sample before use.

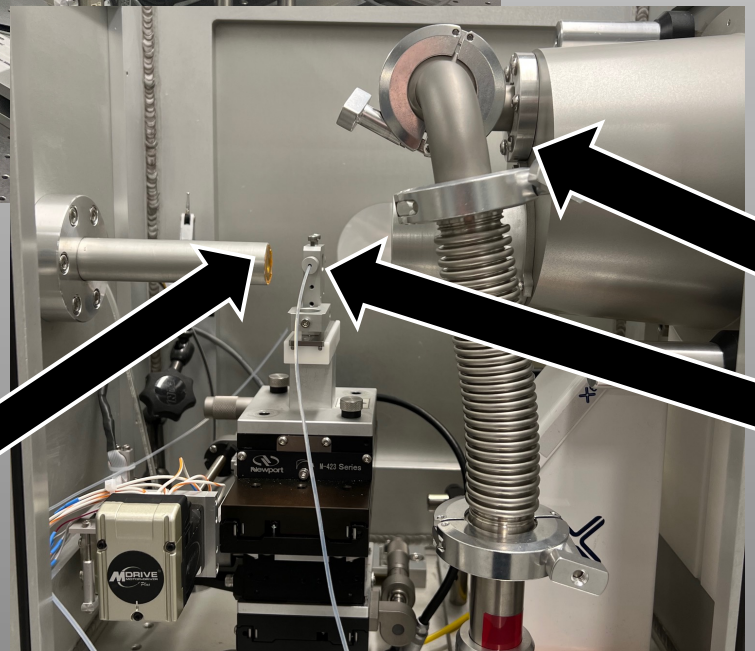
Task 1: Producing and Analyzing Chitin Nano-whiskers

Preparation of Phosphoric Acid Chitin Nanocrystals

- Preparing Reaction Medium:
  - Purified chitin powder + H_3PO_4 (65wt%)
  - Sealed and refrigerated (2-8 °C) for 30 min
  - Centrifuge for 5 min
- Processing:
  - Heat in hot bath, 55°C for 2h
  - Washed with DI and centrifuged 3x (12000 rpm, 10 min)
- Post-processing:
  - Sediment was dialyzed for 48h, pH=6.28
  - The chitin solution was stored at 4 °C.

Task 1: Producing and Analyzing Chitin Nano-whiskers





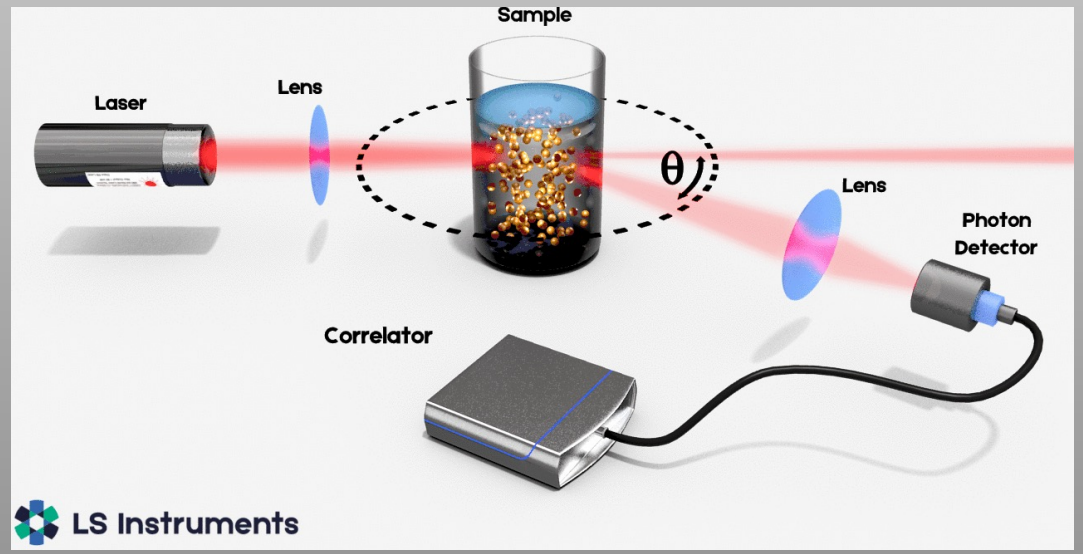
Single Particle Characterization

Small Angle X-ray Scattering

- Located at the UMD X-ray Crystallography Center
- Used to measure **cross sectional size** of ChNWs

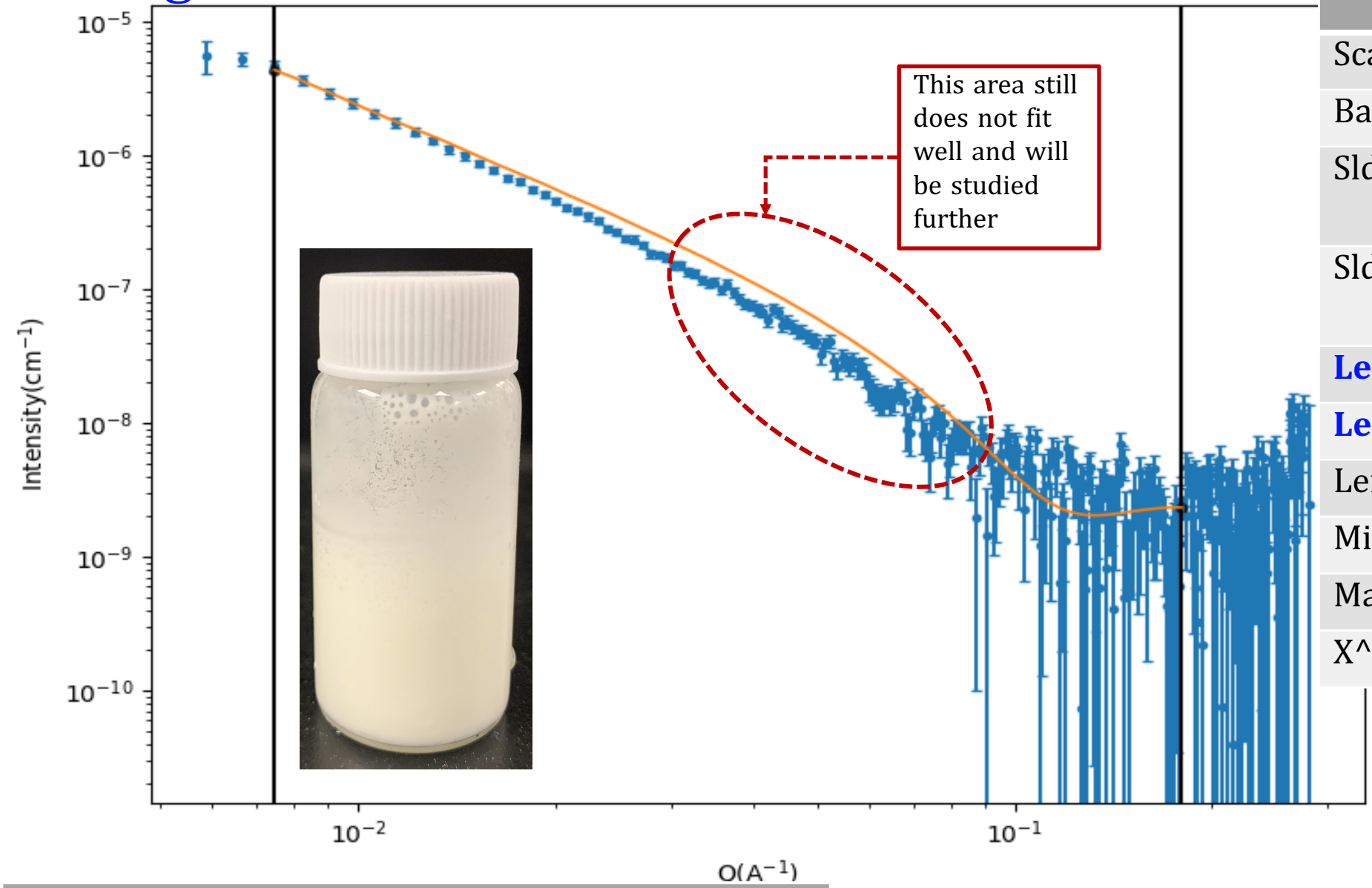
Dynamic Light Scattering

- Used to measure **Length** of ChNWs



https://lsinstruments.ch/en/theory/dynamic-light-scattering-dls/introduction

Single Particle Characterization



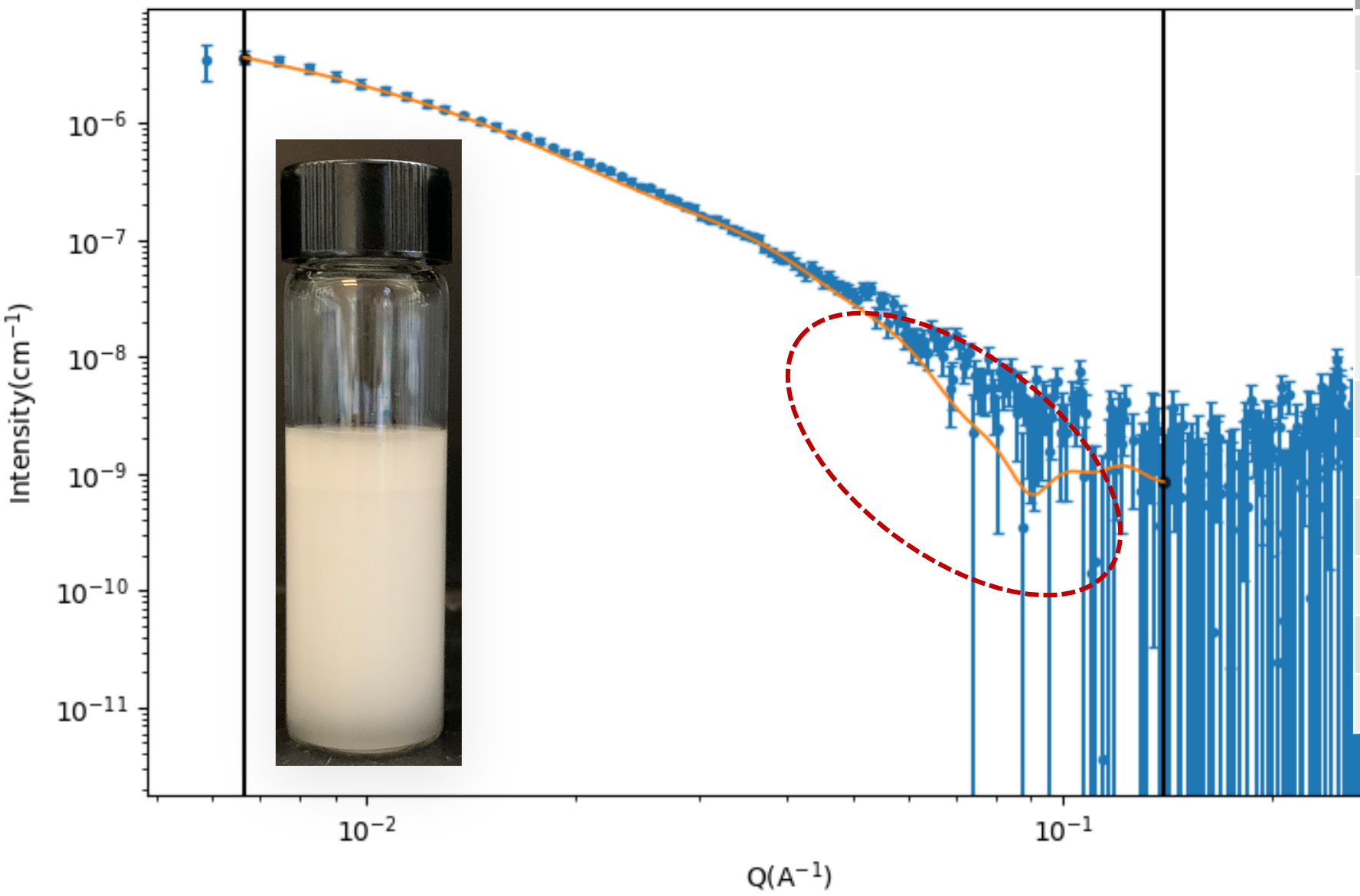
Parameter	Value	Units
Scale	5.9e-10	
Background	2e-09	Cm-1
Sld	13.13	10^-6/Å
Sld Solvent	9.47	10^-6/Å
Length A	**47.809**	**Å**
Length B	**1232.2**	**Å**
Length C	4000	Å
Min range	0.007	Å^-1
Max range	0.18	Å^-1
X^2	1.6e-15	

Weighting – |Data I|
Form factor - Parallelepiped

Parallelepiped Form with lengths a, b, and c.

0.1wt% PA Chitin Emulsion

Single Particle Characterization



Parameter	Value	Units
Scale	3.62e-10	
Background	3.9804e-10	Cm-1
Sld	13.13	10^-6/Å
Sld Solvent	9.47	10^-6/Å
Length A	**70.8**	**Å**
Length B	**282.94**	**Å**
Length C	4000	Å
Min range	0.006	Å^-1
Max range	0.14	Å^-1
X^2	4.7e-09	

Weighting – |sqrt(I Data)|
Form factor - Parallelepiped

0.1wt% TEMPO Chitin Emulsion

Task 1: Producing and Analyzing Chitin Nano-whiskers

Summary of the single particle characteristics from SAXS data and Dynamic Light Scattering

Type of processing ChNW	Cross sectional Area (nm)	Length (nm)
TEMPO ChNW	71x283	139.8+/-10.5
PA ChNW	48x1232	~200

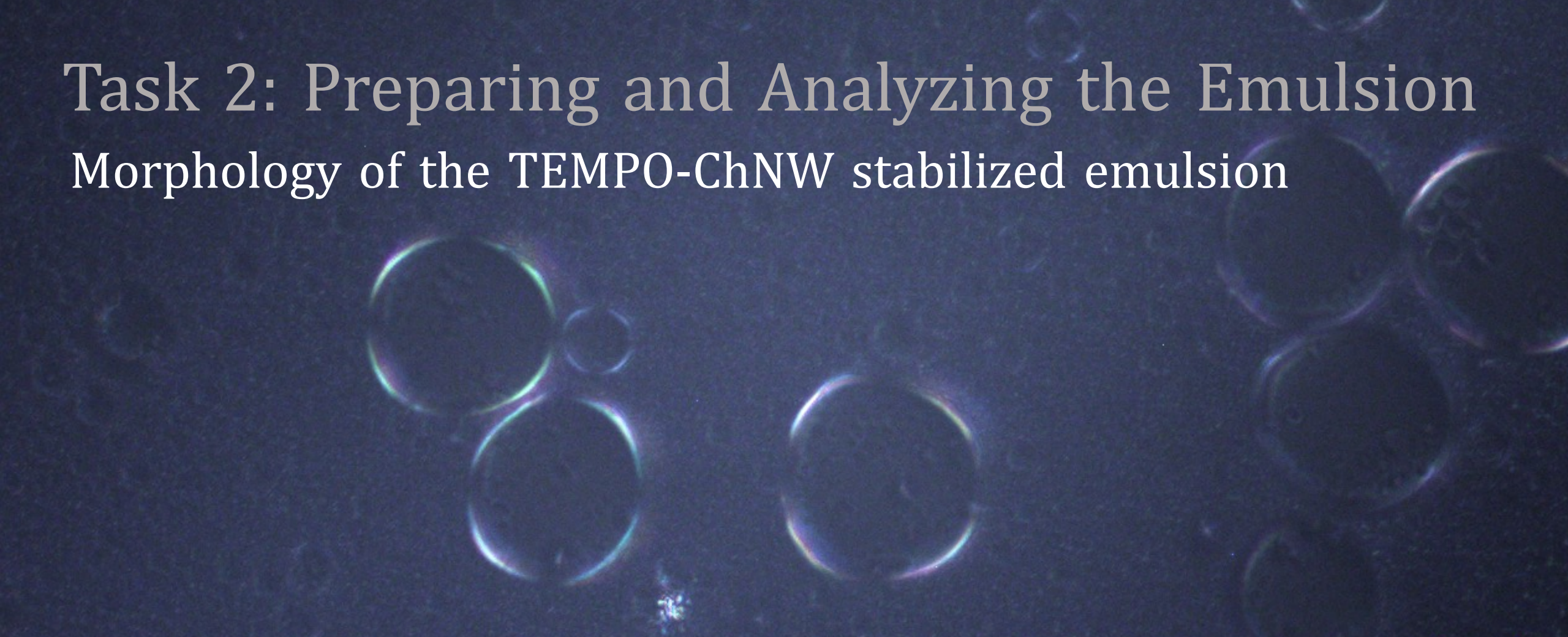
- SAXS data → Cross-sectional area of a single CNW
- DLS → Length of a single CNW

Task 2: Preparing and Analyzing the Emulsion

- 1:9 Oil in Water volume percent + 0.1wt% Chitin
- Sonication to fully disperse oil droplets in the water

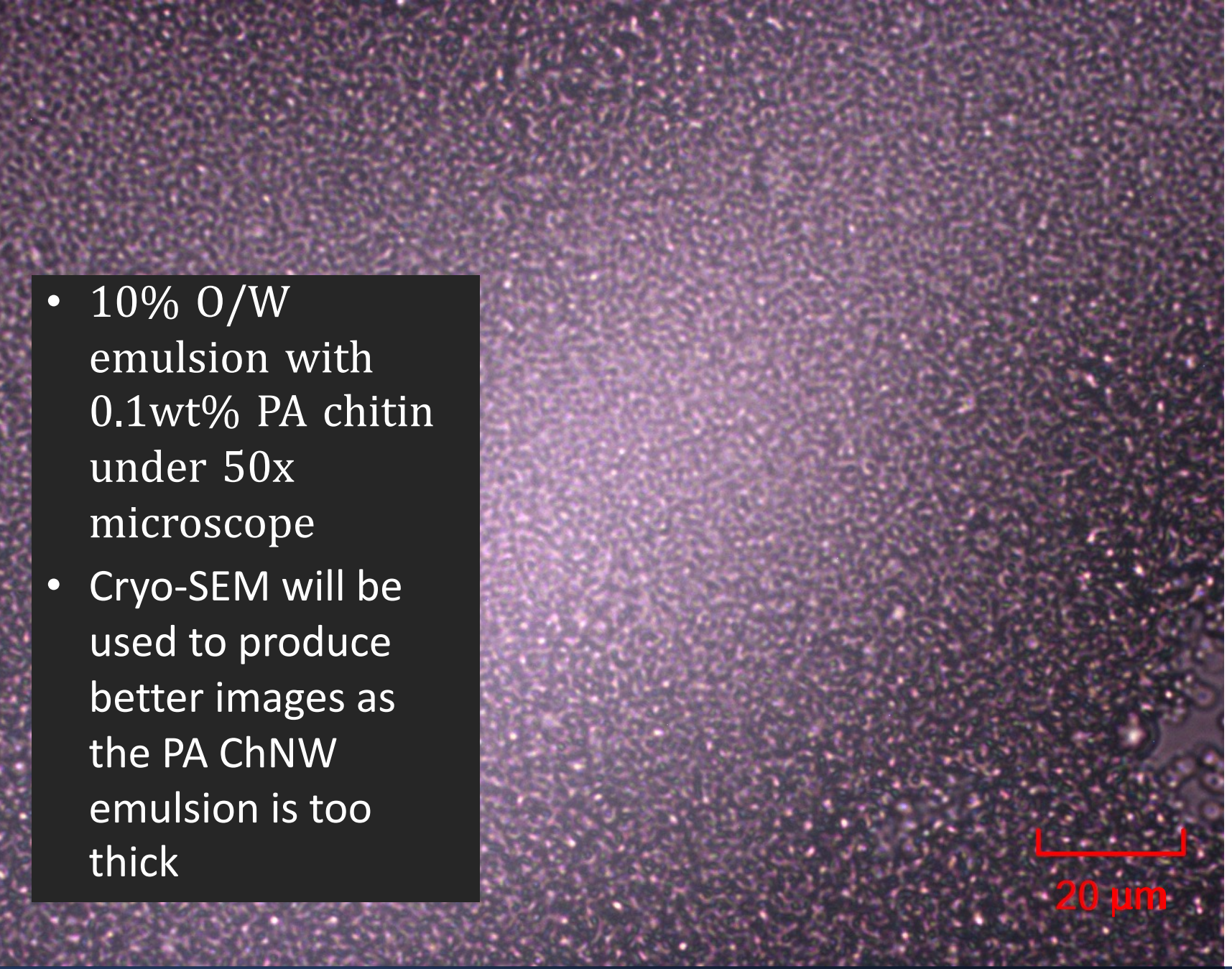
Task 2: Preparing and Analyzing the Emulsion

Morphology of the TEMPO-ChNW stabilized emulsion



10% O/W emulsion with 0.1wt% TEMPO oxidized chitin under 20x polarized light microscope

- The white shining is the chitin nanocrystals acting as colloidal particles surrounding the oil droplets



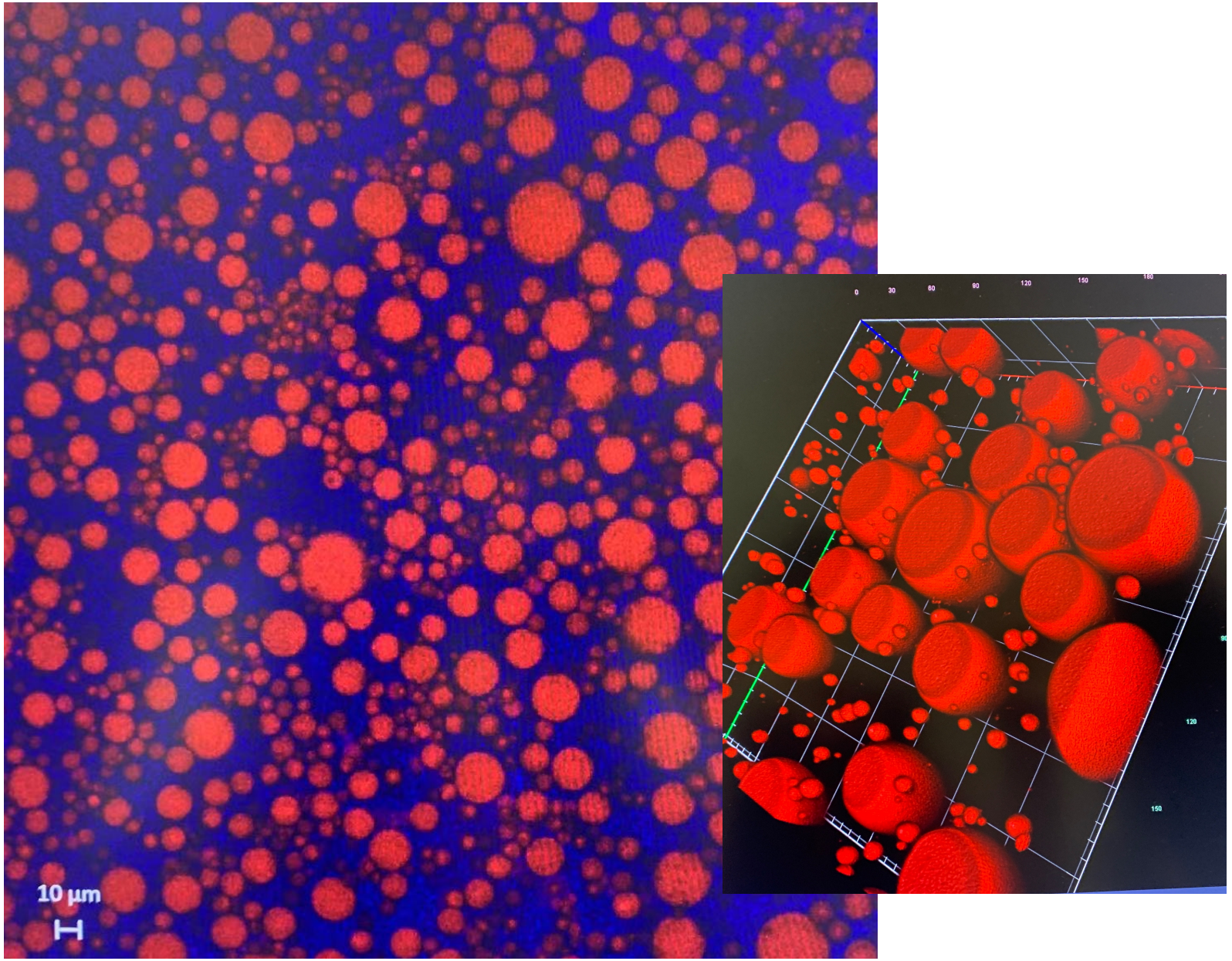
- 10% O/W emulsion with 0.1wt% PA chitin under 50x microscope
- Cryo-SEM will be used to produce better images as the PA ChNW emulsion is too thick

Task 2: Preparing and Analyzing the Emulsion

Morphology of the PA-ChNW stabilized emulsion

Task 2: Preparing and Analyzing the Emulsion

Morphology of the TEMPO-ChNW stabilized emulsion



- 10% O/W Emulsion stabilized by 0.1wt% TEMPO-oxidized ChNW

Conclusion

Type of processing ChNW	Cross sectional Area (nm)	Length (nm)	Microscopy + Confocal
TEMPO ChNW	72x286	139.8+/-10.5	**broad size distribution** ranging from a few microns up to ~20 microns
PA ChNW	48x1709	~200	~2 microns with a relatively **narrow size distribution**

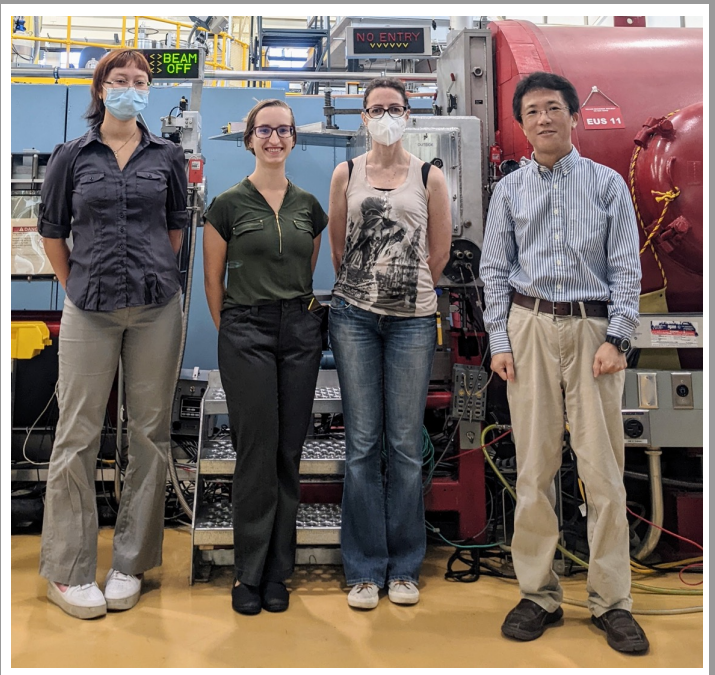
- Reason TEMPO chitin and PA chitin are different → **concentration** and **properties**
- TEMPO is more hydrophilic and more negatively charged so more dispersed

So, what is the next step…

- Use contrast variation techniques with SANS by making the SLD of the oil the same as the water to measure the structure of the chitin in the emulsion in order to be able to **fully characterize** the colloidal particles'

	Calculated Neutron SLD's
MCT Oil	0.215×10-6/Å2
Chitin	2.157×10-6/Å2

- Correlate **the microstructure** of the colloidal particles with **the macroscopic properties** of the Pickering emulsions emulsions to support the design of Food Applications



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