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Fiber Structures from Hydrothermal Treatment of Cellulose Nanocrystals

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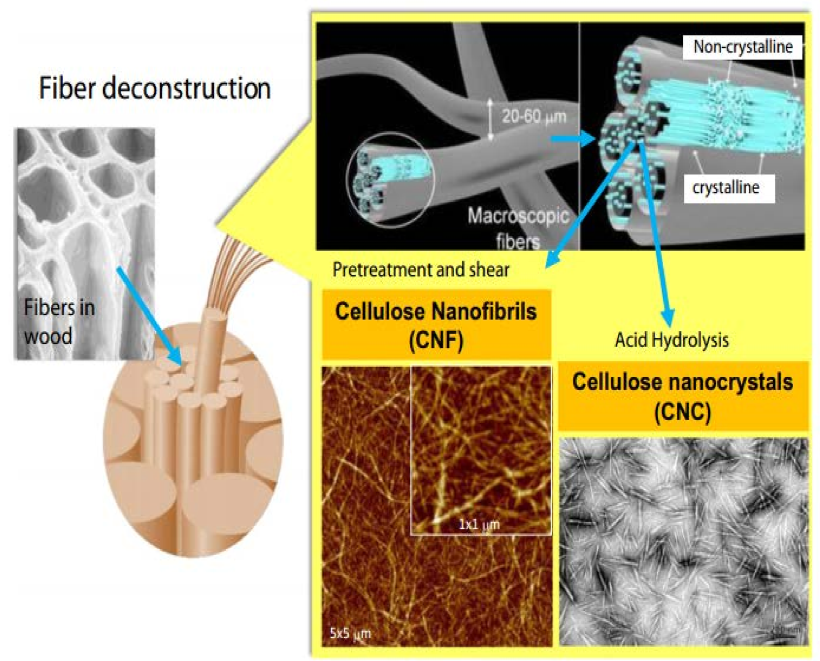
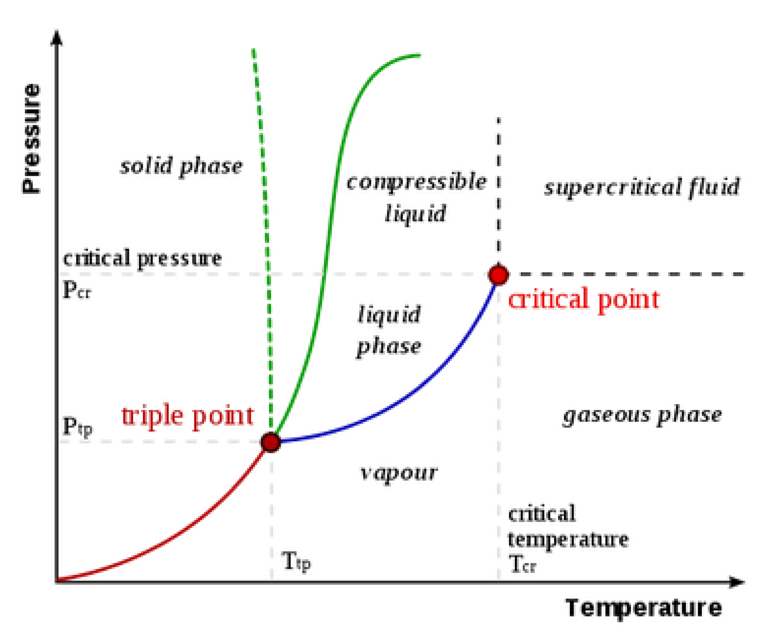
Introduction

Consumers, industry, and government are increasingly asking for materials that are made from sustainable and renewable resources that are plentiful in nature and biodegradable. Natural cellulose based products like wood, cotton and line have been used for thousand years. In a controlled sulfuric acid hydrolysis, cellulose chains in less ordered or amorphous domains can be decomposed leaving the highly crystalline domains intact. These highly crystalline cellulose domains are usually in nanometer wide and 0.1-2μm in length, which are commonly called cellulose nanocrystals (CNC). Derived from the most abundant polymer in nature, CNC is among the most exciting and cutting edge materials. Researchers have reported their applications in reinforcing natural and synthetic polymers, paper coatings and packaging science, as well as potential applications for antibacterial films, liquid crystals, biomedical implants and many others.

In order to fully utilize and understand the science of CNC, we performed a hydrothermal synthesis using cellulose nanocrystals. Hydrothermal synthesis has many advantages over other methods: it's environmentally benign and inexpensive. Superheated water offers high pressure and high temperature with higher diffusivity than liquid phase at the same time providing sufficient density to dissolve materials but keeping low viscosity to facilitate mass transport. To our knowledge, no one has employed the hydrothermal synthesis using CNC as starting material. The chemicals and structures after hydrothermal treatment of CNC are investigated and studied.

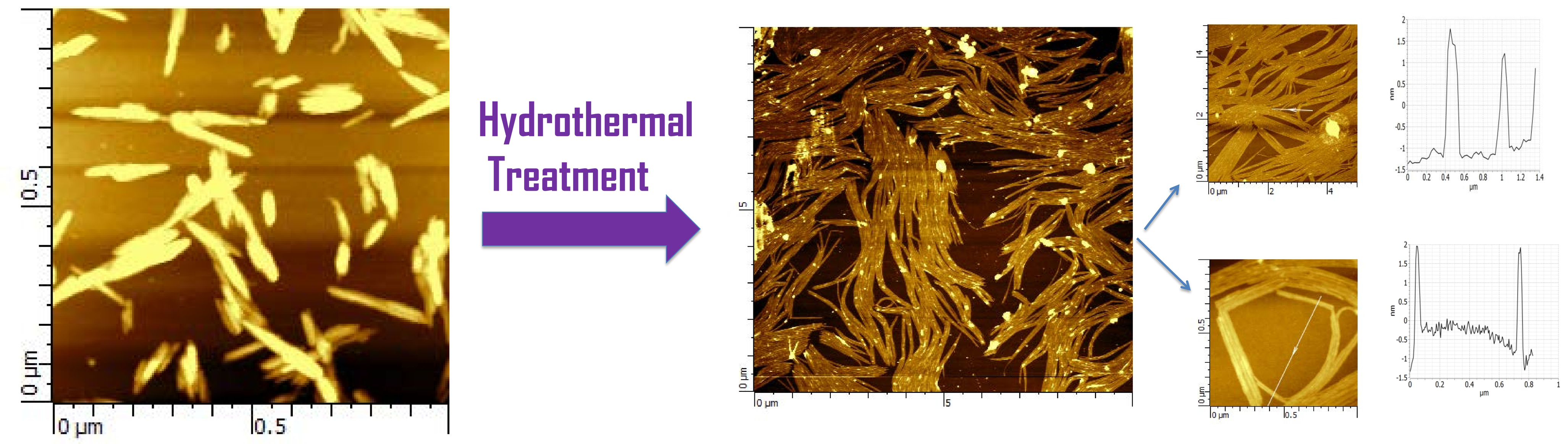


Cellulose Nanocrystals



Phase Diagram

Approach and Methodology:



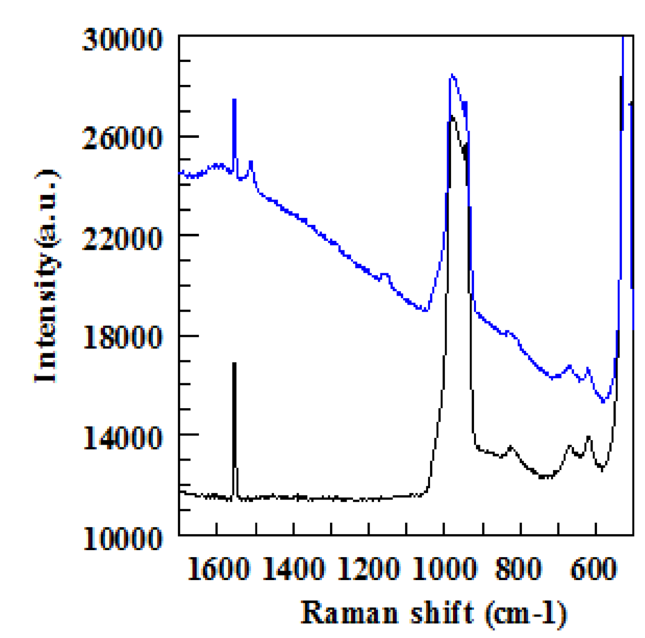
Cellulose Nanocrystals

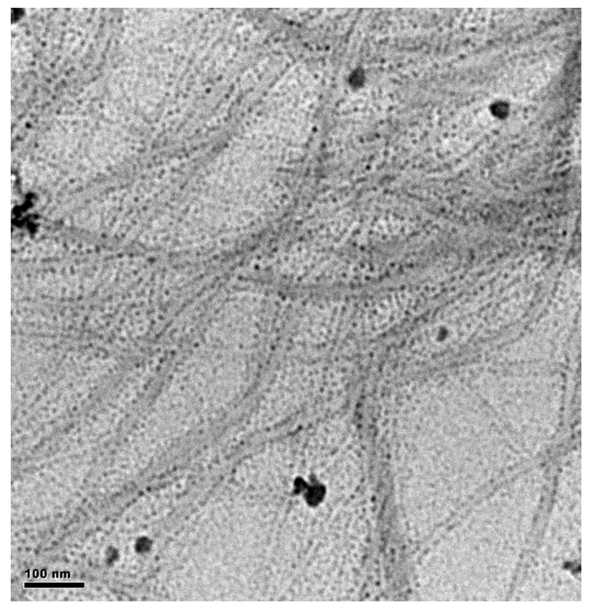
Fiber Structures

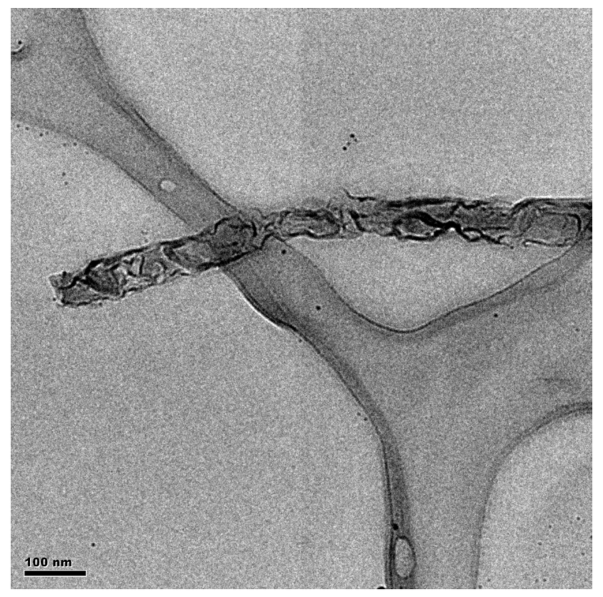
Parameters	CNC	CNC after HTT
Length(nm)	107±55	Tens of micrometers
Width(nm)	20±6	1.5±0.5
Height(nm)	8.9±2.8	1.5±0.5

Comparison of CNC Shape before and after Hydrothermal Treatment

Cellulose nanocrystals showed a squeezed elongated spherical shape under TEM and AFM. After hydrothermal treatment, 1-2 nm in height with micrometer range length fiber structures was found under AFM. In order to define and identify these fiber structures, Raman spectroscopy was measured to obtain more information. An Argon laser with 514.5nm green light was used to excite Raman spectra. (Black-Silicon wafer, Blue-CNC after HTT drop cast on silicon wafer). Compare to silicon wafer, our sample clearly gives two small peaks at 1510 cm^{-1} and 1152cm^{-1} Raman shift, which may be the (9,9), (10, 10) or (11,11)single wall nanotube Raman spectrum according to A. M. Rao's research (Reference 2). Transmission Electron Microscopy(TEM) was done to see the structures in detail. High resolution TEM are still under testing since the contrast between formvar/carbon TEM grid and our fiber are low in the images showed below. We are planning to change or modify the TEM grid to have better resolution images. As it's known that individual carbon nanotubes naturally align themselves into "ropes" (held together by van der Waals forces), more specifically, pi-stacking. Rope structures are reasonable under TEM.







Conclusion and Future Plan

After hydrothermal treatment of CNC, fiber structure materials were found. Preliminary analysis shows the potential of being carbon nanotubes. Carbon nanotubes (CNTs) are among the most exciting new materials being observed and developed. CNTs show superb electronic, mechanical, and structural characteristics providing many applications to new functional devices, such as nanoscale electronic devices, field emission transistors, hydrogen storage devices, etc. CNTs are usually synthesized using laser vaporization, electric arc charge and catalytic chemical vapor deposition, which normally require high energy input and high temperature conditions as well as the need to remove catalysis after synthesis. To our knowledge, nobody has reported the synthesis of carbon nanotubes through hydrothermal treatment of cellulose nanocrystals. Raman spectroscopy shows more distinguishable carbon nanotube peaks and TEM images with distinguishable nanotube structures are under testing. We plan to do further study to determine the surface functionalization of these fibers. Future plans also include focusing on how to purify fibers with the nanoparticles(as we can see from both AFM and TEM images, nanoparticles do exist in and between fiber bundles). The mechanism behind fiber formation also needs to be determined. Research on the precursors for fiber structures will hopefully shine light on how we can use cellulose based or other carbon based material to synthesis carbon fibers through hydrothermal treatment.

Acknowledgements and References

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