Evolution and potential uses of nanocrystalline cellulose

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Introduction

• A very brief outline of the background (with apologies to many people for ignoring their contributions)

• I’m focusing on Cellulose Crystallites or Nanocrystalline cellulose (NCC) or Cellulose Nanocrystals (CNC) (i.e., long-grain rice).

• I’m ignoring the spaghetti-like cellulose nanofibrils (CNF).

• I’m also focusing on optical properties, and ignoring role in strengthening composites, gels and foams
Cellulose intercrystalline structure; study by hydrolytic methods

R. F. Nickerson and J. A. Habrle, (Mellon Institute, Pittsburgh),


“In the hydrolysis of cellulosic fibers with aqueous hydrochloric and sulfuric acids at boiling temperatures, the disordered intercrystalline chain network appears to be attacked first. ……. …..Simultaneously the fibers are reduced to powdery hydrocellulose.”
Aqueous colloidal solutions of cellulose micelles

Bengt G. Rånby (Uppsala University)


X-Ray diffraction on native cellulose indicated crystalline areas or micelles, 60Å x 600Å.

“They have now been obtained in aqueous colloidal solution, and have been observed as isolated morphological units by means of the electron microscope.”

Nanocrystals from cotton (Mukherjee et al., 1952)
Some key publications…

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indicated crystalline areas or micelles, 60Å 
observed in aqueous solutions, 60Å 
have been observed 
by means of m...
A discovery in an apparently unrelated field…

Liquid Crystalline Structure in Aqueous Hydroxypropyl Cellulose Solutions.
R.S. Werbowyj and D.G. Gray


The solutions show the iridescent colours characteristic of a *chiral nematic* (cholesteric) liquid crystal.

Increasing the HPC concentration changed colours from red to blue.

But these colours were for solutions of a *cellulose derivative*!

~55% HPC/water, crossed polars, planar texture with oily streaks
A single (chiral nematic) phase

~45% HPC/water, crossed polars
A suspension of cellulose nanocrystals in pure water at low concentrations forms a clear stable isotropic fluid.

At higher concentrations, the nanocrystals self-align to form a *chiral* nematic liquid crystalline phase in equilibrium with isotropic phase.

**Helicoidal Self-ordering of Cellulose Microfibrils in Aqueous Suspension.**
Quantitative measurements of phase composition and properties of the nanocrystal suspensions were made by graduate student Xue Min Dong and others.
Another unexpected discovery...the chiral nematic order was preserved even on drying the nanocrystal suspension!

Mixture of planchettes cut from cellulose nanocrystal films prepared with different NaCl concentrations, thus giving different reflection wavelengths

Biomimetics: Chiral nematic colour
The colour of the iridescent film depends on illumination, viewing angle and on background.

The same piece of film, photographed...

...under diffuse illumination. ...against a white and a black background.

Film kindly provided by Xuequan Tan, FPInnovations
The chiral nematic nature of the film can be demonstrated by simple optical observations with 3-D glasses.

Butterfly image, made from blue cellulose nanocrystal film.

Viewed through 3-D Glasses (passive, circularly polarized)

The left lens allows only left circularly polarized light to pass.

The right lens allows only right circularly polarized light to pass, and blocks left circularly polarized light.
Iridescent thermotropic chiral nematic made from mixture of cellulose derivatives

Viewed through 3-D Glasses (passive, circularly polarized)

In this case, the chiral nematic structure is right-handed

So passive 3-D glasses can quickly show chiral nematic handedness

Chiral Nematic Mesophases of Lyotropic and Thermotropic Cellulose Derivatives.
Chiral nematic structure clearly shown by SEM of fracture surface

This pattern is an oblique cross-section of a chiral nematic assembly of cellulose nanocrystals.

see Majoinen, Kontturi, Ikkala and Gray, *Cellulose* (2012) 19:1599–1605
Iridescent films are likely to be a niche application.

But the novel properties, and preparation from wood pulp led to a growing interest:

• Changing name from “cellulose crystallites” to “cellulose nanocrystals” didn’t hurt.

• Building on earlier work, a family of nanocellulosic materials was soon developing.

• Work at STFI (now Innventia), KTH and Aalto University demonstrated promising properties of longer nanofibrils (NFC) prepared mechanically (Tom Lindstrom et al.) and chemically at University of Tokyo (A. Isogai et al.)
The self assembly and attractive optical properties drew attention to the CNC nanomaterial.

Other properties were also attractive:
  • In principal, cellulose is an abundant and relatively cheap raw material
  • A renewable, green, nontoxic product
  • The CNC are high crystallinity, high modulus, colorless and strong.

But, until recently only available in small lab-scale quantities.

However, as Dr. Berry from CelluForce will describe, CNC is now available in developmental quantities.

Many proposed applications!
NANOCELLULOSES  A somewhat overlooked family of nanoparticles

Why is this? Perceptions....

• Of no interest to chemists
• Boring chemistry; a long string of glucose units
• Worse, chemists have failed to be able to synthesis cellulose in any reasonable quantity
• Covalent modification of cellulose seems trivial
• Photonically and electronically uninteresting (spin correlation length <1 nm)
Reality:
• Cellulose is a critical component of the biosphere
• Every second of daylight, megatons of cellulose are being synthesised by green plants.
• Obviously, this is the ultimate green process...
• One can make a family of nanocrystals from the cellulose provided by green plants
• The products are renewable, non-toxic, almost carbon-neutral, with interesting mechanical properties
• Cellulose nanocrystals do self-assemble to give interesting optical and magnetic properties.
Fundamental research priorities may depend on applications priorities!
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Historically, working on CNC preparation and properties:-
  Julie Giasson, (Ph.D. 1995, TEM and microscopy)
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  Catherine Edgar (Ph.D. 2002, phase separation, surface properties)
  Maren Roman (PDF, 2004, film structure)
  Stephanie Beck (Ph.D. 2006, phase separation of mixtures)
  Emily Cranston (Ph.D. 2008, multilayers)
  Elisabeth Kloser (PDF, 2009, modification)
  Tiffany Abitbol (Ph.D. 2011, cellulosic nanostructures)
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Thanks!