Chapter 1

Cellulose Nanocrystals – A Material with Unique Properties and Many Potential Applications

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Introduction

Cellulose nanocrystals (CNCs) are cellulose-based nanoparticles that can be extracted by acid hydrolysis from a wide variety of natural source materials (e.g., trees, annual plants, tunicates, algae, bacteria) [1-7]. These rod-like or whisker-shaped particles (Fig. 1, 3–20 nm wide, 50–2000 nm long) have a unique combination of characteristics: high axial stiffness (~150 GPa), high tensile strength (estimated at 7.5 GPa), low coefficient of thermal expansion (~1 ppm/K), thermal stability up to ~300°C, high aspect ratio (10–100), low density (~1.6 g/cm^3), lyotropic liquid crystalline behavior, and shear-thinning rheology in CNC suspensions. The exposed –OH groups on CNC surfaces can be readily modified to achieve different surface properties and have been used to adjust CNC self-assembly and dispersion for a wide range of suspensions and matrix polymers and to control interfacial properties in composites (e.g., CNC-CNC and CNC-matrix). This unique set of characteristics results in new capabilities compared to more traditional cellulose-based particles (wood flakes, pulp fibers, etc.) and the development of new composites that can take advantage of CNCs' enhanced mechanical properties, low defects, high surface area to volume ratio, and engineered surface chemistries. CNCs have been successfully added to a wide variety of natural and synthetic polymers [2] and have been shown to modify composite properties (mechanical, optical, thermal, barrier). Additionally, CNCs are a particularly attractive nanoparticle because they have low environmental, health, and safety risks, are inherently renewable, sustainable, and carbon-neutral like the sources from which they are extracted, and have the potential to be processed in industrial-scale quantities at low costs.

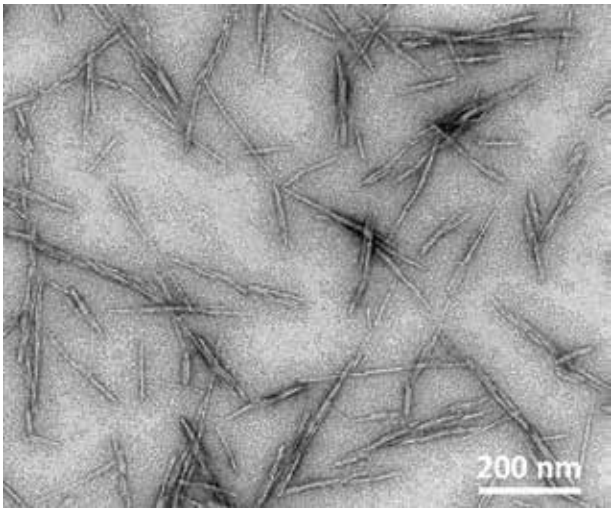

Figure 1. *Transmission electron microscopy (TEM) image of CNCs extracted from microcrystalline cellulose.*

Processing of Cellulose Nanocrystals

Although there are many variants of the process to isolate CNCs from a given cellulose source material, this process generally occurs in two primary stages. The first stage is a purification of the source material (plants, tunicates, algae, bacteria, etc.) to remove most of the non-cellulose components in the biomass. These include lignin, hemicellulose, fats and waxes, proteins, and inorganic contaminants. The second stage uses an acid hydrolysis process to deconstruct the "purified" cellulose material into its crystalline components. This is accomplished by preferentially removing the amorphous regions of the cellulose microfibrils [3,8]. The resulting whisker-like particles (3–20 nm wide, 50–2000 nm long) are ~100% cellulose, are highly crystalline (62%–90%, depending on cellulose source material and measurement method), and have been referred to in the literature as cellulose nanocrystals (CNCs), nanocrystalline cellulose (NCC), and cellulose nanowhiskers (CNW) to name a few. The variations in CNC characteristics (e.g.,

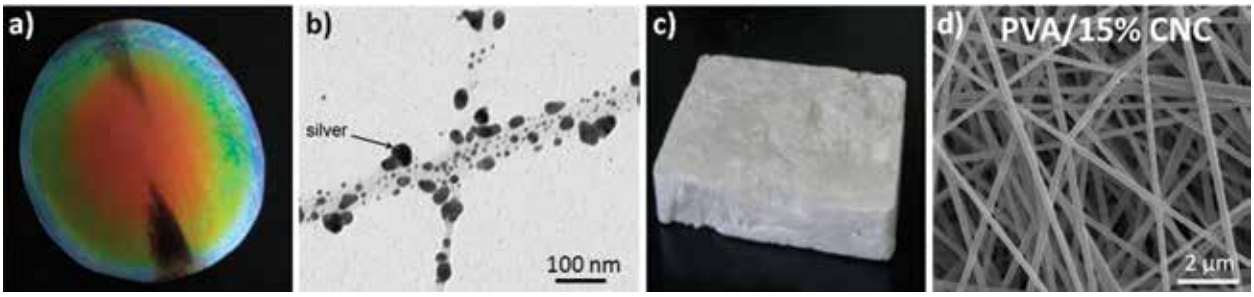

Figure 2. *a) Photograph of CNC film showing iridescent/pearlescent optical behavior [courtesy of FPInnovations], b) TEM image of a tunicate CNC surface functionalized with silver nanoparticles[16], c) Photograph of CNC foam [courtesy of Shaul Lapidot, Hebrew University of Jerusalem, Israel], d) Scanning electron microscopy (SEM) image of 15wt% CNC-polyvinyl alcohol (PVA) electrospun continuous fibers [courtesy of Prof . Orlando Rojas [15]].*

particle morphology, surface chemistry, percent crystallinity, etc.) are strongly linked to the cellulose source material and the acid hydrolysis processing conditions. Subsequent chemical treatments can be carried out to alter the CNC surface chemistry.

CNCs are a particularly attractive nanoparticle because they have low environmental, health, and safety risks, are inherently renewable, sustainable, and carbon-neutral like the sources from which they are extracted, and have the potential to be processed in industrial-scale quantities at low cost.

Research Areas in Cellulose Nanocrystals

Research on CNC materials covers a wide range of topics, including, but not limited to, CNC extraction processes, CNC suspension (dispersion, modification, liquid crystallinity, rheology, etc.), CNC surface functionalization (chemical, polymer grafting, nanoparticles, metal cations, DNA, etc.), CNC structural and property characterization, CNC composite processing (self-assembly, dispersion, network formation, interface engineering, films, continuous fibers, foams, etc.), CNC composite properties (mechanical, optical, thermal, barrier properties, etc.), predictive modeling (multi-length scale, structure, properties, etc.), life-cycle analysis, and environmental health and safety. Many of these topics will be covered in subsequent summaries within this section of the book.

Potential Applications

Potential applications of CNCs can be loosely grouped based on some unique combinations of CNC characteris-tics; several of these are listed below.

Rheology modifiers. Addition of CNCs can alter the rheology [9] of various media (liquids, polymer melts, particle mixtures) that are used in many industrial applications, such as paints, coatings, adhesives, lacquers, food, cosmetics, drugs, and cements.

Reinforcement for Polymer Materials. Addition of CNCs to various polymer matrix materials alters the mechanical properties of the resulting composites and can be used in the development of robust, flexible, durable, lightweight, transparent, and dimensionally stable films which may be used in packaging or structural composite applications.

Barrier Films. CNC-based composites incorporating tailored CNC surface chemistry and spacing between CNCs have attracted interest as barrier films with potential uses in selective filtration, batteries, and packaging applications [2-4,6].

Optical Films or Coatings. The liquid crystallinity of CNC suspensions, coupled with the birefringent nature of the particles, leads to interesting optical phenomena

The exposed –OH groups on CNC surfaces can be readily modified to achieve different surface properties, and have been used to adjust CNC self-assembly and dispersion for a wide range of suspensions and matrix polymers and to control interfacial properties in composites

which can be exploited for the development of iridescent/pearlescent optical behavior for unique optical patterning of surfaces (Fig. 2a) [5,9,10].

CNC-Hybrid Composites. CNC composites that integrate inorganic nanoparticles (or chemical species) onto CNC surfaces (Fig. 2b) and/or into CNC networks have added chemical functionality which could be of use in biosensors, catalysis, photovoltaics, drug delivery, filters, and antimicrobial applications [4,6].

CNC Foams. CNC foams (e.g., aerogels) are highly porous materials (densities = 0.01–0.4 g/cm^3, surface area = 30–600 m^2/g) [11–13] and could be used in lightweight packaging, lightweight core-skin structures, and thermal or vibration insulation applications (Fig. 2c).

CNC Continuous Fibers. Continuous CNC-composite fibers (Fig. 2d) have been produced through typical fiber spinning techniques (e.g., electrospinning, dry and wet spinning) [14,15] and could be used in textile development and long and short fiber-reinforcement applications.

Summary

The unique set of characteristics of CNCs and CNC suspensions and the recent advances in CNC production capability have accelerated fundamental and applied research and development of CNC materials for a number of industrial applications. In the following pages, scientists working with CNCs will summarize aspects of their research on the properties and applications of this fascinating material.

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Acknowledgments. The authors acknowledge Shaul Lapidot and the laboratory of Prof. Oded Shoseyov, the Faculty of Agriculture, Food, and Environment, Hebrew University of Jerusalem, and Melodea Ltd. for the photograph of the CNC foam, and Prof. Orlando Rojas of North Carolina State University for the SEM image of CNC-polymer fibers.

Production and Applications of Cellulose Nanomaterials

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Cellulose nanocrystals incorporated within the overcoat varnish of the cover!

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ISBN: 978-1-59510-224-9
TAPPI PRESS Order Number: 0101R332
Printed in the United States of America