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MACROMOLECULAR 1D CRYSTALLINE NANO-ARRAYS FOR HIERARCHICAL STRUCTURES AND FUNCTIONAL MATERIALS

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Nanocelluloses are highly crystalline (65%-95%) rod-like nanocrystals or fibril-like nanofibrils that can be isolated from cellulose of diverse origins, including tunicate, algae, bacteria and wood [1]. Cellulose nanocrystals are typically 4 to 20 nm wide with 20-100 aspect ratios. The bending strength and modulus of celulose nanocrystals have been estimated by Raman spectroscopy to be ~10 GPa and ~150 GPa, respectively [2]. This impressive bending strength is about one-seventh of that for carbon nanotubes and far higher than Kevlar. With extensive inter-molecular and intra-molecular hydrogen bonds among equatorial primary C6 and secondary C2 and C3 hydroxyls and absence of free rotation along β-(1→4)-glycosidic linked D-anhydroglucopyranose, cellulose is highly crystalline, strong and rigid, making it challenging to dissolve and engineer as macromolecules. Nanocelluloses present unique crystalline structure and surface chemistries to be versatile building blocks for superior and sustainable materials.

This presentation highlights a range of approaches to derive 1D nano-arrays of highly crystalline nanocellulose in varied geometries and surface chemistries from which new structures and functional materials are created.

We have developed streamlined processes to isolate cellulose from under-utilized agricultural and processing byproducts. Pure cellulose has been isolated from rice straw [4], grape pomace [5] and tomato peel [6]. Cellulose nanocrystals (CNCs) and nanofibrils (CNFs) can be derived *via* sulfuric acid hydrolysis, mechanical blending and TEMPO-mediated oxidation [7]. Sulfuric acid hydrolysis produces highly crystalline (up to 90.7% CrI) 3.96-6.74 nm wide, 116.6-166 nm long CNCs with similarly negative surface charges (-44 to -38 mV) and sulfate contents. Mechanical defibrillated CNFs are 82.5% crystalline and bimodally distributed in sizes (2.7 nm wide and 100-200 nm long; 8.5 nm wide and micrometers long). TEMPO mediated oxidation liberated the most uniform, finest (1.7 nm) and longest, but least crystalline (64.4% CrI) CNFs [4]. Combined TEMPO oxidation and mechanical shearing improves nearly 100% yield [5].

All nanocelluloses have cellulose Iβ crystalline structure and are more crystalline than its source. The surface charges on CNFs may be tuned to allow assembling into other controlled hierarchical structures. Rapid freezing induces self-assembly into nanometer to sub-micron wide fibers while slow freezing induces ice-crystal templating to generate hydrogels and aerogels [8]. Most significantly, these ultra-lightweight (1.7 mg/cm^3) and highly porous (99.9% porosity) aerogels are amphiphilic, absorbing 250-300 mL/g of aqueous as well as non-polar hydrocarbons. Aerogels may be tuned to be oleophilic super-absorbents, excellent for selective hydrocarbon and oil recovery [9].

CNFs have also demonstrated as dual capping and shape-regulating agent for the synthesis of silver nanoparticles as well as nanoprisms. CNFs significantly improve the stability and dispersibility of

Ag nanoparticles in physiological medium, validating the antimicrobial potential of CNF-AgNPs, and providing insights on the physio-chemical interactions between bacteria and CNF-AgNPs in a physiological growth médium [10]. Ag nanoprism bound CNFs have shown excellent surface enhanced Raman scattering of Rhodamine 6G with analytical enhancement factor of $5x10^3$ for potential applications as senors [11].

Other novel functional nanocelluloses [12-15] as well as assembled hybrid structures will also be presented. Furthermore, full utilization of biomass is realized by advanced carbon byproducts such as activated carbon nanofibers for supercapacitors.

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