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Regular Article

Functionalization of cellulose nanocrystals for advanced applications

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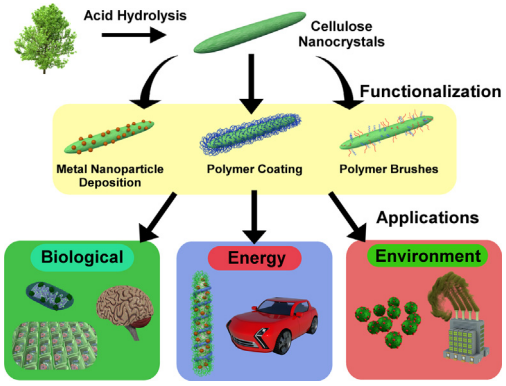
GRAPHICAL ABSTRACT



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ABSTRACT

Replacing the widespread use of petroleum-derived non-biodegradable materials with green and sustainable materials is a pressing challenge that is gaining increasing attention by the scientific community. One such system is cellulose nanocrystal (CNC) derived from acid hydrolysis of cellulosic materials, such as plants, tunicates and agriculture biomass. The utilization of colloidal CNCs can aid in the reduction of carbon dioxide that is responsible for global warming and climate change. CNCs are excellent candidates for the design and development of functional nanomaterials in many applications due to several attractive features, such as high surface area, hydroxyl groups for functionalization, colloidal stability, low toxicity, chirality and mechanical strength. Several large scale manufacturing facilities have been commissioned to produce CNCs of up to 1000 kg/day, and this has generated increasing interests in both academic and industrial laboratories. In this feature article, we will describe the recent development of functionalized cellulose nanocrystals for several important applications in ours and other laboratories. We will highlight some challenges and offer perspectives on the potentials of these sustainable nanomaterials.

Abbreviations: CNCs, cellulose nanocrystals; NFC, nanofibrillated cellulose; SANS, small angle neutron scattering; HIPE, high internal phase emulsion; DMAB, didecyldimethylammonium bromide; CTAB, cetyltrimethylammonium bromide; PDMAEMA, poly(dimetheylamino ethylmethacrylate); POEGMA, poly(oligoethylene glycol) methacrylate; PMAA, poly(methacrylic acid); PNIPAM, poly(N-isopropylacrylamine); HEC, hydroxyethyl cellulose; PAAM, polyacrylamide; POM, polarized optical microscopy; TEOS, tetraethyl orthosilicate; TMOS, tetramethyl orthosilicate; TEOT, titanium(IV) ethoxide; UF, urea-formaldehyde; PVA, poly(vinyl alcohol); PAMAM, poly (amidoamine); MF, melamine-formaldehyde resin; PR, polyrhodanine; PVP, poly(N-vinylpyrrolidone); CSos, chitosan oligosaccharide; IMI, imipramine hydrochloride; PrHy, procaine hydrochloride; DOX, doxorubicin; PEEP, poly(ethyl ethylene phosphate); VC, vitamin C; FITC, fluorescein-5′-isothiocyanate; RBITC, rhodamine B isothiocyanate.

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1. Introduction

In nanoscience and nanotechnology, the synthesis and modification of nanomaterials with well-defined structure and functionalities have attracted growing interest due to their many potential applications [1,2]. Recent advances in nanomaterials have led to the development of functionalized nanoparticles that hold promise in various industrial sectors, such as medicine, electronics, biomaterials and energy production [3,4]. However, a large proportion of chemicals used to produce nanomaterials are derived from petroleum-based resources, and they involve the use of toxic reagents that are harmful to the environment. Due to concerns on global warming and sustainable development, there is an urgent need to replace traditional raw material supply with those derived from renewable resources [5]. Furthermore, the ability to transform cheap and abundant material to yield high value products will offer significant advantage.

It is well-known that cellulose is the most abundant naturally occurring polymer found in this planet [6]. It represents about 1.5×10^{12} tons (metric tonne) of total annual biomass production and is considered an inexhaustible source of raw material capable of meeting the increasing demand for environmentally friendly and biocompatible products [6,7]. Economical and environmentally friendly methods have been developed to process cellulosic materials by dissolving them in NaOH/urea solution or ionic liquids, as reported by Zhang's [8–10] and Rogers' laboratories [11,12], respectively. Unfortunately, the approach of disassembling cellulosic materials to their molecular entities sacrifices the attractive physical properties of the crystalline domains formed by the inter- and intra-molecular hydrogen bonds. By careful control of the disassociation of amorphous regions while retaining the crystalline domains, a new form of crystalline cellulose commonly referred to as nanocellulose is produced [7]. These nanocelluloses have size in the nanometer regime, and they possess many attractive characteristics, such as versatile fiber morphology, hydrophilicity, easy surface modification, large surface area and high aspect ratios [7]. Depending on their dimensions, origins and processing conditions, nanocellulose can be divided into two main categories, namely cellulose nanocrystals and cellulose nanofibrils. In this feature article, we will focus mainly on cellulose nanocrystals, however reviews on cellulose nanofibrils can be found in several recent publications [7,13–16].

2. Cellulose nanocrystals

Cellulose nanocrystals (CNCs) are the crystalline domains extracted from wood fiber through acid hydrolysis. They are rigid, rod-like particles with a width of several nanometers and lengths of up to hundreds of nanometers [17,18]. The microscopic properties (physical and surface chemistry) of CNCs have an important bearing on their macroscopic properties (rheology, colloidal stability, etc), and these are summarized in Fig. 1.

2.1. Physical properties

The main physical dimensions for cellulose nanocrystals include the length (L), diameter (D) and aspect ratio (L/D), which are dependent on the source of cellulose or hydrolysis conditions (acid type, reaction time and temperature). CNCs derived from wood and cotton are usually shorter than that obtained from tunicate and bacterial cellulose because the latter possess a higher degree of crystallinity [17,18]. Lower fractions of amorphous regions make them more resistant to degradation from acid hydrolysis resulting in larger rod structures. Typically, the aspect ratio ranges from 10–30 for CNCs derived from cotton and up to approximately 70 for tunicate. Sulfuric and hydrochloric acids are the most commonly used acids in the hydrolysis process, but other strong acids, such as phosphoric and hydrobromic acid have also been reported [14,17]. Different acids may lead to significant differences in the dispersity and colloidal stability of CNCs. For instance, CNCs derived from sulfuric acid hydrolysis disperse readily in water due to the abundance of negatively charged sulfate ester groups on their surface, while aqueous solutions of CNCs produced from hydrochloric acid hydrolysis display poor colloidal stability [18]. In addition to the properties discussed above, cellulose nanocrystals also possess other attractive features: large surface area (250–500 m^2/g), and improved mechanical strength (tensile strength 7500 MPa and Young's modulus of 100–140 GPa)[19]. The extremely high Young's modulus is an attractive characteristic for application in nanocomposites. Liquid crystalline behavior has also been observed for non-flocculating cellulose nanocrystal suspensions. In the dilute solution regime, CNCs are isotropic, and at higher concentrations the nanoparticles align to form an anisotropic nematic phase [17]. Beyond this critical concentration, CNC dispersions display shear birefringence, and they can spontaneously phase separate into an upper isotropic and a lower anisotropic

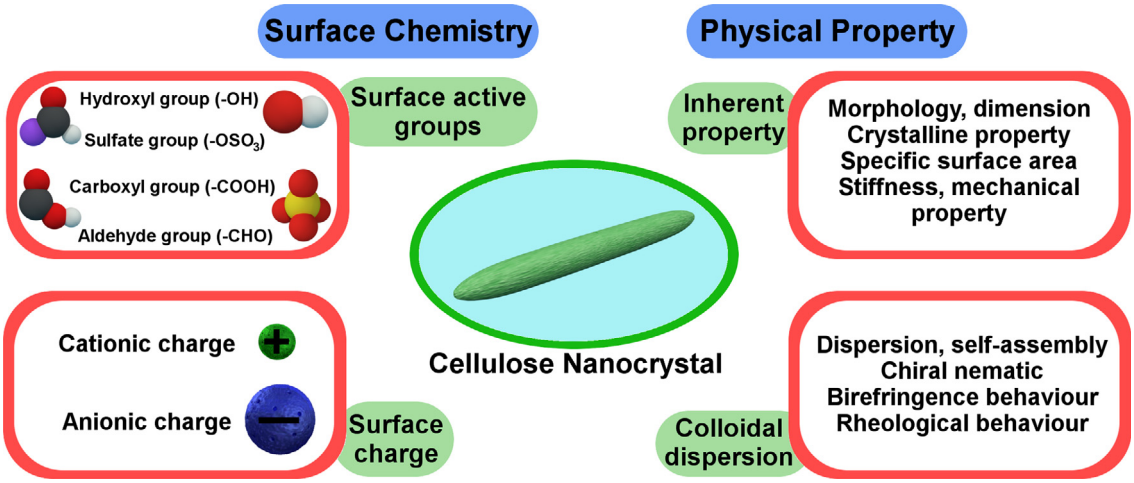

Fig. 1. A summary of the physical and chemical properties of cellulose nanocrystals.