

COMMENTARY

Designing nanocellulose materials from the molecular scale

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Cellulose, in the form of cellulose nanocrystals, cellulose nanofibrils, or bacterial cellulose, has emerged as a renewable material with countless potential applications in materials science and engineering (1). Its anisotropy and excellent mechanical properties, together with its biocompatibility and tunable surface chemistry, have made cellulose-based nanomaterials a cornerstone in a new generation of sustainable materials from biomass. Accordingly, extensive experimental efforts, assisted by multiscale modeling techniques, have been devoted to better understand structure–property relationships of nanocellulose materials (2). In PNAS, Molnár et al. (3) provide a molecular dynamics study on the atomic deformation mechanisms of cellulose crystals under different loading conditions to expand our fundamental knowledge on the mechanical properties of these nanocrystals, which is essential to truly unlock the potential of cellulose-based nanomaterials in engineering applications. The complex structure of cellulose crystals at the nanoscale influences the properties of cellulose materials at the macroscale level; therefore, fundamental understanding of nanoscale mechanisms through multiscale modeling provides guidelines for the bottom-up design of cellulose-based nanomaterials, based on structure–property relationships and future modification and shaping of cellulose (4) (Fig. 1).

Cellulose chains self-assemble into helicoidally oriented fibrils that organize themselves into structures of higher order, resulting in a layered arrangement. This self-assembled structure resembles those observed in collagen, chitin, or DNA (5), with a helical conformation that maximizes energy dissipation through crack bridging, deflection, and twisting (6). Crack deflection slows down crack propagation, crack twisting allows multiple cracks to grow without coalescing, and crack bridging minimizes stress concentration at the crack tip. Modeling and simulating these mechanisms help in the development of technologies to control them. Furthermore, hydrogen bonds stabilize the cellulose crystals, while the continuous covalent bonding along the nanofibrils provides stiffness and strength.

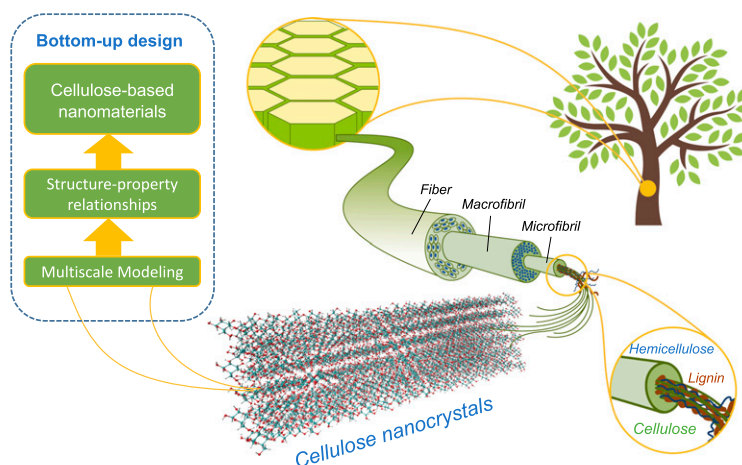


Fig. 1. (Right) Schematic representation of the hierarchical structure of lignocellulose biomass down to cellulose nanocrystals. **(Left)** Diagram shows how the atomistic model of cellulose nanocrystals is the starting point for the bottom-up design of cellulose-based nanomaterials.

This abundance of hydrogen bonds and the length of molecular chains hamper the dissolution of cellulose and boost the search for solvents to successfully utilize cellulose at larger scales (7). Despite scaled-up processing challenges, remarkable advances have been achieved in biomedicine (8), energy (9, 10), printed electronics (11), and infrastructure applications (12), although many fundamental questions about the structure and nanoscale behavior of cellulose crystals are still open. In biomedicine, more insights into self-assembled cellulose-based systems for trapping hydrophobic drugs, fluorescent probes, and biomolecules are still needed (8). In energy applications, controlling the intermolecular interactions within cellulose crystals is expected to provide new material formulations for energy harvesting and storage (9), including solar energy devices, supercapacitors, and lithium-ion batteries (10). In the case of printable electronics, the behavior of cellulose crystals under shearing conditions is crucial for the implementation of inks with nanocellulose conductive particles; therefore, molecular-scale

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mechanisms like those provided by Molnár et al. (3) are essential to develop advanced technologies that incorporate spinning, 3D printing, or microfluidics into the manufacturing process. Moreover, the impact of a better understanding of the mechanical properties is even more clear in the case of infrastructure applications, in which cellulose crystals have been incorporated into building materials to improve mechanical performance under loading conditions while meeting lightweight demands (12). Despite the variety of applications, the alignment, anisotropy, and mechanical properties under different loading directions determine the performance of cellulose crystals. Thus, fundamental knowledge about the nanoscale behavior of these crystals under shear stress is important to all these applications.

In this regard, tensile properties have been the main focus for studies about the mechanical performance of cellulose nanocrystals (13), which, as it has already been mentioned, are arranged in a helical conformation stabilized by hydrogen bonds in a stacked, layered architecture. This molecular structure implies the existence of privileged directions of deformation, which are those that mainly involve weak nonbonded interchain interactions rather than stiffer intrachain covalent bonds. At the very fundamental level, Molnár et al. (3) highlight the importance of the shear mode of deformation occurring at stress levels lower than tension with much larger ductility. This effect is essential beyond the elastic domain, for which available studies are still scarce. Thus, these authors have focused their study in these preferential directions that involve noncovalent interactions to force cellulose chains to slide along their faces either perpendicularly or parallel to their long axis, and to induce sliding of the chains along their side. By doing this, they have been able to evaluate the elastoplastic shear deformation of cellulose crystals, and its dependency on shearing directions in which noncovalent interactions are critical. The atomic-scale mechanisms elucidated by these means show that cellulose crystals behave as hyperelastic media up to the point of plastic instability. Furthermore, they demonstrate for the first time how defects drastically facilitate plasticity. In fact, the presence of dislocations does not alter the initial linear elastic regime, but they glide and induce plastic deformation at a critical stress.

This fundamental understanding should spark new studies on the atomic-scale mechanisms of cellulose crystals and cellulose nanocomposites to guide the development of more accurate

manufacturing techniques for biomass-derived nanomaterials that are designed from the molecular scale. Properties such as dispersion, distribution, and alignment of the reinforcing phase are affected by stresses during the manufacturing process (14), and multiscale simulations provide computational tools to predict stress distribution and its effects on macroscopic properties. Techniques for manufacturing materials with nanoscale features that incorporate oriented nanofibrils and nanocrystals are being implemented for cellulose-based materials, and complex mechanisms that incorporate electric fields or magnetic fields can lead to the formation of 2D materials, such as membranes and nanopapers. Additionally, new manufacturing techniques that incorporate nanocellulose by an extrusion process induce hydrodynamic forces in the cellulose fibrils, which align along the printing direction. Understanding the fundamental mechanisms of these crystals under shearing conditions will guide the implementation of anisotropic printed structures with enhanced mechanical stability.

Important fundamental questions related to the overall stress/strain response of cellulose crystals, anisotropy of deformation, nanoscale mechanisms, and shearing orientation can be answered from the mechanistic insights at the atomic level that Molnár et al. (3) provide. In fact, these molecular dynamics simulations prove that shearing perfect cellulose crystals beyond linear elasticity is highly nonlinear and anisotropic, while dislocated cellulose exhibits an elastoplastic behavior similar to metallic crystals. As stated by these authors, additional investigations are needed to better understand the plasticity of cellulose crystals. In the meantime, these fundamental insights pave the way for future studies on the effect of crystal size, shearing directions, and surface effects to provide stronger foundations for bottom-up beam models (15). The development of better multiscale models and more accurate atomistic simulations is expected to provide further understanding of the underlying mechanisms that control the behavior of nanocellulose along different length scales. This knowledge, in combination with available techniques in nanotechnology and additive manufacturing, has the potential to revolutionize the future of biomass-derived materials.

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