Tuning the Interfacial Chemistry of (Nano)Cellulose for the Fabrication of Advanced Materials and Devices

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Cellulose has been used throughout history as a source of building materials, textiles, and paper products due to the unique mechanical and chemical properties that arise from its hierarchical organization. Through research, we are learning that crystalline nanocelluloses (*i.e.*, cellulose nanocrystals – CNCs, and cellulose nanofibrils – CNFs) not only exhibit the expected enhanced mechanical properties, but also display unique optical, electric, piezoelectric, and magnetic properties that are not found in macroscale cellulosic materials. These unique properties, along with their biodegradability and cytocompatibility, make nanocelluloses excellent candidates for the development of new advanced and environmentally benign materials. However, one of the most pressing challenges for the widespread deployment of nanocelluloses is the lack for simple routes to confer to them a wide range of surface functionalities. Our group has pursued innovative modular surface chemistry approaches, directed towards hydroxyl or carboxylate groups, that allow us to tune the interfacial properties and reactivity of a broad range of cellulose nanomaterials.

This presentation will describe our efforts aimed at developing a range of small molecules that can be easily grafted onto cellulosic materials to convey a broad range of functionalities. First, I will describe the use of triazinyl chemistry as a simple and versatile way to efficiently modify the primary hydroxyl groups of cellulose.[1] Using this chemistry it is possible to render cellulose hydrophobic, fluorescent, or reactive. Examples of the use of triazinyl surface modifications to create hydrophobic paper structures[1], to tag nanocellulose with organic dyes to study its intrinsic nanostructure,[2] to functionalize 3D printed structures,[3] and to create ultraporous scaffolds will be discussed.[4,5] Next, I will describe the use of a bifunctional azetidinium for the selective modification of oxidized celluloses. Carboxylated nanocellulosic materials present better dispersion in polar solvents than native celluloses and offer the possibility of targeted functionalization with controlled degrees of substitution. However, currently most surface functionalization of carboxylated nanocelluloses is performed through processes that are expensive or require multiple lengthy steps. Our group has pursued modular azetidinium surface functionalization approaches allow us to tune the interfacial properties and reactivity of a broad range of carboxylated cellulose nanomaterials. Examples of the use of these surface modifications to tag nanocelluloses with organic dyes for high-resolution fluorescence microscopy, to modify paper properties, and to create ultraporous silicone-cellulose composite materials will be presented. I will end with an overview of our most recent work using azetidinium-modified celluloses to develop a range of new 3D printable hydrogel resins

The ability to tune the interfacial chemistry of cellulosic materials with simple and efficient reactions opens the door for the use of these functional sustainable materials in a range of applications, including environmental monitoring and remediation, paper-based microanalytical devices, and 3D printing, among many others. In addition, the ability to apply such modular approaches to functionalize other polysaccharides make them attractive routes for the development of green materials and composites with unique properties and functionalities.

References

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Figure 1. Schematic showing the functionalization of 3D printed structures through adsorption of reactive nanocellulose. Reproduced from Reference 3.

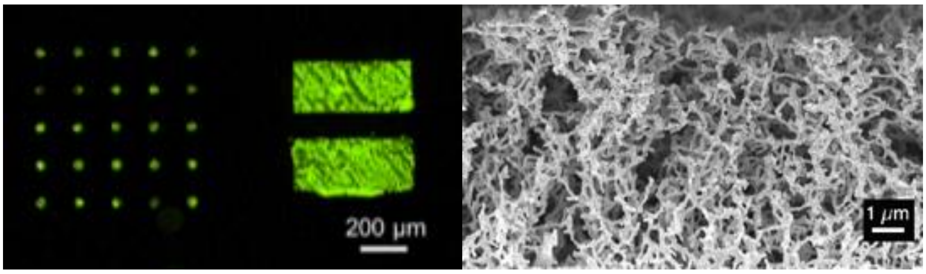

Figure 2. Photographs of patterned ultraporous scaffolds made from reactive nanocellulose. Reproduced from Reference 5.