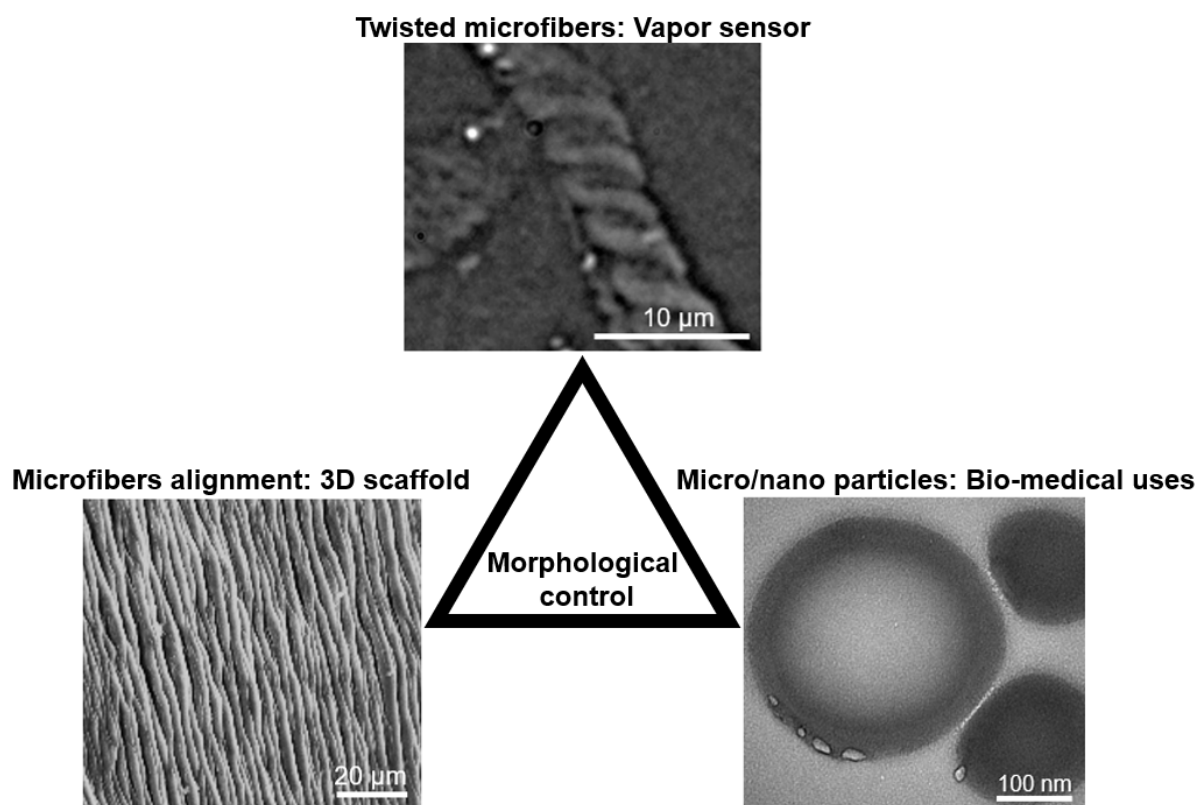


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Abstract

Morphological control of self-organized body on supergiant polysaccharides

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Graphical abstract

In materials design, the relationship between polymer morphology and physical properties is crucial. The researchers are attempting to utilize alternative materials such as natural biopolymers to limit the consumption of non-renewable resources produced by synthetic materials. In recent decades, there has been an increased interest in the utilization of polysaccharides, particularly bioactive ones, for various novel applications owing to their biocompatibility, non-toxicity, and

some specific therapeutic activities. The biological activities of polysaccharides are strongly affected by their chemical structure and chain conformations. The morphological control of polysaccharides from nano to micrometer scale has seldom been utilized in vitro because of the difficulties in regulating self-assembled structures. Herein, it is demonstrated that a cyanobacterial polysaccharide, *sacran*, could hierarchically self-assemble as twisted fibers from the nanoscale to microscale with diameters of $\sim 1 \mu\text{m}$ and lengths $>800 \mu\text{m}$, that are remarkably larger than polysaccharides previously reported. Unlike other rigid fibrillar polysaccharides, the *sacran* fiber was capable of flexibly transforming into two-dimensional (2D) snaking and three-dimensional (3D) twisted structures at an evaporative air-water interface. It was determined that the microfiber had a diameter of $\sim 1 \mu\text{m}$ and formed of a self-assembled torsional structure of nanofibers with diameters of $\sim 50 \text{ nm}$. This structure was stable in pure water. Upon adding monovalent cations such as Na^+ from NaCl , the microfiber is capable of disassembling into submicrometer-scale particles. The microfibers tended to integrate into a uniaxially oriented state along the contact line of the evaporative air-water interface. When one side of the microfibers was fixed, they drastically transformed into 2D snaking and 3D twisted structures. The velocity of the contact line movement during drying affected the structure formed because of the capillary forces at work between the microfibers. The evaporative air-water interface also induced multi-twisted structures to form from multiple microfibers, thereby showing that this material has self-similar nano and microstructures. The snaking and twisted fibers made possible a film exhibiting millisecond-response repulsive motion to water vapor. By introducing functional molecules into the microfiber, it would be possible to prepare a variety of soft actuators responding to other changes in the external environment, such as light, pH, and temperature. The method for preparing vapor sensors developed by this study not only improves understanding of how the motion of self-assembled

structures responds to stimuli but also contributes towards the design of environmentally adaptive materials with a high potential for sustainable use. We envision that this approach is capable of reconstructing additional natural materials towards developing advanced microsensors. Moreover, the scaffold of highly oriented M-fibers was successfully prepared. This could be an excellent place to start looking into cell orientation in relation to M-fibers for the new material design.

Moreover, the deformation process of *sacran* microfiber to nano-micro particles was also clarified in vice versa. The interaction between polymer chains is an essential component in studying *sacran* morphological change. The microfibers deformed to particles by reducing the intermolecular interaction, for example, the dilution and the salination. In case of decreasing concentration to the semi-diluted state ($c < c_e$ 0.015 wt%), the polymer would be in the unentangled state which is unable to form microfiber. At the concentration of 0.010 wt%, the microfibers significantly deformed into the nanofibers and nanofragments. This could be the boundary concentration of nano to micro assembling process. After that, the salination effect was studied as another factor that suppresses the interaction between the polymer chains. Sacran at a diluted state (0.001 wt%) with 10 mM of NaCl added, the salting-in affected on higher solubility of polymer chains. Then, 100 mM of NaCl was added, the salt affected on less soluble of the polymer referred to the salting-out. This effect could produce the *sacran* particles with a very narrow size distribution. However, the dilution and the salination method conferred a small quantity of particles because the particle would be formed with narrow size distribution under a very low polymer concentration or with a crucial high concentration of salt. That problem could be overcome by the ultrasonication technique. At polymer concentration 0.010 wt%, the *sacran* microparticles are successfully prepared. Sonication plays a vital role in polymer scission and spherical shape formation through cavitation. The overall treated ultrasonic energy directly affects the size of the particles.

Consequently, the polymer particles were annealed, aiming to get microparticles gel for further applications. For instance, the *sacran* microgel represented super-moisturizing ability comparative to other currently used materials. This would be a significant investigation of a new polysaccharide particle because the preparation processes are ultimately simple and non-necessity of organic solvents nor artificially synthetic molecules, they would be the alternative option in the green chemistry. Furthermore, the Sacran microparticles could be modified for additional applications such as microgel drug carrier or intranasal spray for moisture maintaining. Base on the outstanding properties of the prepared, this study could lead to a new material design for medical purposes in the future.

Keywords: Polysaccharides, self-assembly, fibers, particles, drying.

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