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ABSTRACTS (PH D THESIS)

Studies on Structural Analysis, Self-Organizing Capacity and Disassembly of Nanocelluloses

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Cellulose is naturally provided as the crystalline nanofibers with a high tensile stiffness, a high elastic modulus and a low coefficient of thermal expansion (e.g., in the case of cellulose I crystalline, 3~6 GPa,[1] 140~150 GPa,[2] and 10^{-7} K^{-1},[3] respectively). Since various methods and techniques have been developed to produce "nanocelluloses (NCs)", the potentials of NCs for various materials were accordingly developed. Still, there are several major but fundamental issues arising in utilization of NCs as nanomaterials: the length and shape estimation of long and coiled nanofibers having bundles or branches, the shape-dependent self-organizing capacity for fibrous materials, and so on. In this thesis I developed the novel approach by introducing the evaporation induced self-assembly (EISA) techniques to analyze the structures and self-organizing behaviors for nanocelluloses.

"Coffee ring method": Semiquantitative structural analysis for nanocelluloses[4]

A coffee ring (a ring-shaped deposition of colloidal particles) is readily observed when a coffee drop dries on a table. This EISA occurs largely because of the pinning of the contact line of the droplet by the deposited particles, and the outward capillary flow to the contact line generated by the regional change in the evaporation flux.[5] I focused on the differences in the excluded volume effects induced by the anisotropy of nanocelluloses during enrichment, which produced the different packing fractions in the rings.

Three kinds of cellulose nanoparticles (CNPs) were prepared; cotton nanowhiskers (CNWs), tunicin nanowhiskers (TNWs), and sugi nanofibers (SNFs). Both whiskers were produced via acid hydrolysis using H_2SO_4, and sugi pulp was fibrillated using a grinder to obtain SNFs. Transmission electron microscope (TEM) observation was able to measure the precise size distribution for CNWs and TNWs, whereas the long and coiled SNFs were unable be measured. To estimate the length of SNFs, I thus formed the coffee rings for each CNP suspensions on the cleaned glass plates.

Each ring exhibited the obviously different width in the same concentration of nanocelluloses, as shown in Figure 1. To detect the excluded volume effects for nanocelluloses, I measured the ring width normalized by the ring radius (w/R) against the suspension concentration (Figure 1d). The plots had the logarithmic relation for each sample, showing the different excluded volume effects. I analyzed these plots by computing the ring volumes, and developed the theoretical method to simultaneously estimate the shape and length. The method revealed that the SNF units were coiled in a steric structure with a small apparent aspect ratio and with the same volume as a sphere of

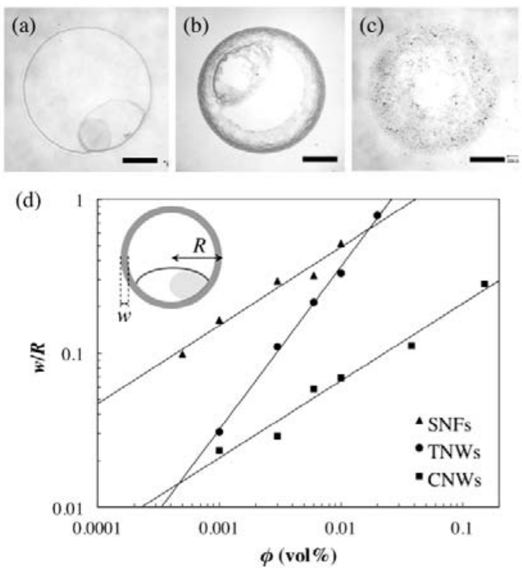

Figure 1. Optical micrographs of (a) CNW, (b) TNW, and (c) SNF stains left on the substrate after the evaporation of a 1 μL droplet of a 0.01 vol% suspension. Note 500 μm scale bars in lower right corners. (d) The width of the ring (w) at depinning normalized by the droplet radius ($R \approx 1$ mm) vs the concentration ( ). A best fit to a power law gave an exponent of 0.51±0.01 for the SNFs, 0.50±0.01 for the CNWs, and 1.06±0.01 for the TNWs. The inset shows the schematic illustration of a typical CNW coffee ring, with twice depinning.

radius 693.22 nm, with 1.08 wt %; the length was estimated as 11.33 μm. This coffee ring method allows semiquantitative volume information to be determined, owing to the excluded volume of particles; this permits a semiquantitative estimation to be made of the length of highly anisotropic colloids, as long as the Debye length is determined for the colloids in question. This method also allows the effective size and the conformational structure of colloids in different systems to be compared.

Self-organizing capacity of nanocelluloses via droplet evaporation[6]

The great potential of nanofibers, for applications to functional materials, provides a strong motivation to understand the relation between the shape and the self-organizing capacity of these particles, and the processes by which they can be made to form higher-order structures. Since the fibril-like shape can be determined through the coffee ring method, I then explored the self-organizing behavior for different shaped nanocelluloses.

I succeeded in producing the semi-flexible nanofibers (TNFs) and rod-like nanowhiskers (TNWs) from the same origin of tunicate cellulose. Both nanocellulose suspensions were subjected to the EISA system in 2D (coffee ring formation) for determining the shape and length, and in 3D (spray drying) to form the microparticles to observe the autonomously-expressed assembly.

EISA results in 3D were found to be consistent with those in 2D for both TNWs and TNFs. The rod-like TNWs formed unexemplied curved discotic MPs by self-organized nematic bundles during spray drying, as displayed in Figure 2, whereas the semi-flexible TNFs formed flattened MPs, albeit with multiple sharp kinks and rough contours. The rod-like nanocelluloses exhibited the self-organizing capacity of the phase transition and left-handed chirality to form MPs with nematic rings along the contours. On the other hand, the semi-flexible nanofibers with a *w*/*R* value of 0.91 failed to align or to undergo a phase transition by EISA system. The expression of the self-organizing capacity of rod-like particles was found to be independent of initial droplet shapes and sizes via surface tension measurements.

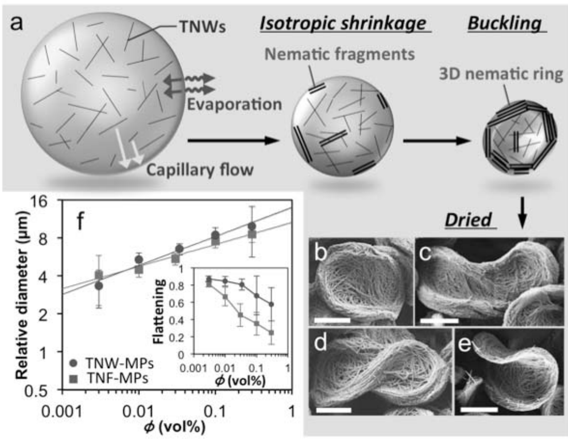

Figure 2. (a) Schematic illustration of the EISA process in 3D during spray drying for rod-like TNWs. Nematic rings in TNW-MP sprayed at ≤ 0.034 vol% formed circular discs (b), "peanut-shaped" (c) or "figure-eight-shaped" (d) structures, and curved discotic shapes (e) (scale bars: 1 μm). The relation between the size and concentration ( ) showed a power-law dependence (f). The inset shows the flattening of MPs decreased (became closer to the spherical) as the particle size increased. Data are means ± SD of ~20 measurements.

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