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Application for beam time at ESRF – Project Description

In-situ monitoring of cellulose dope in microfluidic chanel during the spinning process of high performance fiber

Proposal Summary:

We discovered that microfluidic channel with multiple flow focusing by diluent and coagulant inlet leads to continuous regenerated cellulose fiber with exceptional mechanical properties from aqueous lithium hydroxide system. We will study the orientation and coagulation of cellulose in the microfluidic channel using simultaneous small- and wide-angle X-ray scattering in-situ. The molecular orientation, density fluctuation and coagulation/crystallization will be analyzed at different loci of the microfluidic channel to understand the mechanism leading to the exceptionally high mechanical properties produced by the microfluidic spinning. The process involves extension of dope in a focusing flow field, diffusion of coagulant into the dope and crystallization/phase separation in to the dope, which can be monitored by combining small-angle scattering, transmission, wide-angle solution scattering and diffraction signals.

Scientific background:

Aqueous sodium hydroxide is an attractive solvent of cellulose for its low environmental impact and low cost but the fiber properties spun from such dope had limited mechanical properties preventing its use for wide structural applications. Indeed, standard wet spinning technology do not allow fiber drawing since the regeneration bath immediately forms a skin layer on the surface. In our recent study, we found that continous fibers with ultra-toughness (162 $MJ \cdot m^{-3}$) can be produced using microfluidic spinning. The microfluidic with focusing allows elongational flow field that are in general more suitable for inducing a high uniaxial alignment. Indeed obtained fiber showed highly aligned fibrous objects in the core and showed high uniaxial orientation in X-ray small angle scattering and diffraction. However we do not know at which point in the microfluidic channel, the high orientation was achieved and the its timing with respect to the coagulation process.

X-ray scattering technique has already applied for a similar flow-focus microfluidic system to study the alignment of cellulose nanofibers[1-3]. Our system is a little bit more complex as it involves multicomponent solvent and coagulation process. On the other hand we have already analyzed the coagulation process in a static diffusion process at D2AM, where the coagulant diffusion, density fluctuation in the dope and crystallization of cellulose could be separately analyzed by combining transmission, small angle signal, diffraction signal and solution scattering profiles over wide q-range[4].

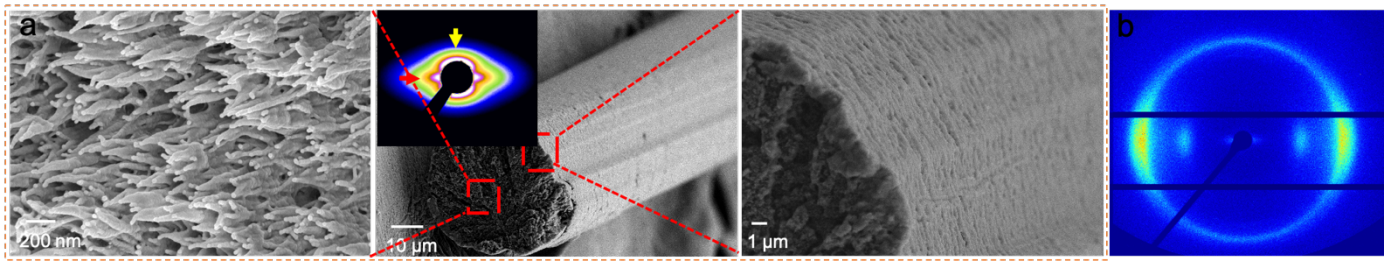

Fig. 1 Microstructure of regenerated cellulose fibers produced in microfluidic cell. a) scanning electron micrograph and small angle X-ray scattering in the inset; b) Wide-angle X-ray scatteing of the corresponding fiber bundle.

Experimental plan:

The microfluidic system is built in Wuyi University and will be brought to the beamline. The proposer, Xiaotong Fu will be hosted at CERMAV (France) for 12 months as part of the PhD project. The X-ray scattering experiment will be carried out at the D2AM beamline. Two silicon pixels detectors WOS and D5 will be used simultaneously to cover wide Q-range. Microfluid system will be mounted on a sample stage with translational freedom. The channel (1 mm) is sandwiched between two glass plates (totally 200 µm).

Typical experimental conditions are: the core flow of cellulose-LiOH/Urea dope with flow rate 200 µL/min, and 1st sheath flows will be aqueous LiOH/Urea solution with flow rate of 400 µL/min and 2nd sheath flow of phytic acid (pH will be 1.53) at a flow rate will of 200 µL/min. The microfluidic system will be translated to probe different loci of the microfluidic channel (Fig. 2).

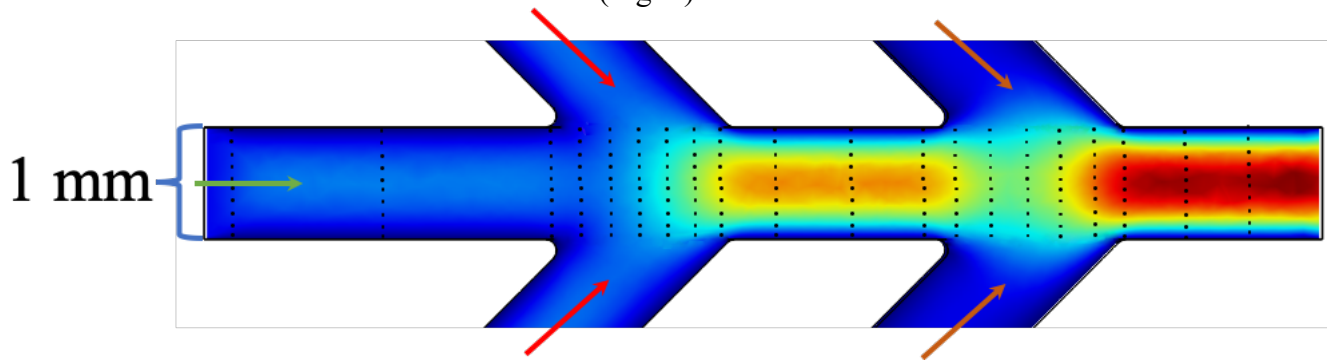

Fig. 2. Geomtry of microfluidic device and positions for X-ray scattering experiment.

Beamline(s) and beamtime requested with justification:

This X-ray scattering experiment will be carried out at the D2AM beamline of the ESRF, which has a simultaneous SAXS-WAXS capacity with large a sample environment area. The study needs a well-controlled and focused beam with reasonable brilliance to map the scattering signal on the microfluidic chip. We require 1 shift for mounting and aligning the microfluidic device, we probably need relatively long exposure time of one minute per point to get good statistics to subtract background. 10 x 20 points on the microfluidic would require 4 hours for each condition. We want to study two sets of flow rates and two types of diluent sheath and two types of alkali (LiOH and NaOH) leading to 8 conditions in total. With some overhead in changing between conditions, we would need 6 shifts in total.

Results expected and impact - analysis strategy and significance of the results:

The data will be analyzed using custom made program. The position of each pixels will be mapped into polar coordinates in reciprocal space. Since in this experiment the detector setting is unique, a sorted reference file will be created once so that a q-range and azimuthal angle range of interest can be quickly accessed from the array of intensity data, and treated as 3 dimensional dataset (q, azimuthal angle, intensity), allowing a direct fitting to model funcions.
The molecular orientation is expected to give anisotropic signal at intermediate q-range, while the coagulation of cellulose and density fluctuation would give strong central scattering. If the coagulated structure is oriented, this signal will be anisotropic from which orientation function can be directly obtained. A crystal growth type coagulation will lead to a power law decay of q^{-4}, while density fluctuation such as spinodal decomposition would give some shoulder signals. Crystal growth can also be monitored in the wide angle scattering as appearance of diffraction peak, whose orientation can be again quantified because we are covering the whole azimuth with the WOS detector.

References

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