

# Dynamic characterization of cellulose nanofibrils

**Zhe Yuan, Jinsong Zeng and Kefu Chen**

State Key Laboratory of Pulp and Paper Engineering, Plant Micro/Nano Fiber Research Center, School of Light Industry and Engineering, South China University of Technology, Guangzhou 516640, China.

Email: fezengjs@scut.edu.cn

**Abstract.** We have carried out dynamic characterization of cellulose nanofibril in micro fluidic chip because nanoscale cellulose has been widely used in various fields. We finally achieved a rapid and accurate measurement of cellulose nanofibril by building the platform include optical microscope, CCD camera and micro fluidic chip. This new measurement method is simple and convenient to operate, and the amount of sample data is large enough to make the data more credible.

## 1. Introduction

Cellulose nanofibril(CNF) generally refers to a cellulosic material having at least one nanoscale dimension, ie, between 1-100 nm[1]. Cellulose nanofibril has many unique properties that are different from those of micron or millimeter-sized cellulose fibers, which makes them useful in a wide range of applications, such as reinforcing agents and rheology modification[2-4]. Like any new nanomaterial, the correct characterization of CNF is very important for its application. However, the dynamic characterization of CNF is very difficult because of its fiber morphology and heterogeneity in the liquid.

The sizes of CNF with large ratio of length to diameter need to be characterized on multiple scales. At present, the characterization of CNF mainly depends on electron microscopy and atomic force microscopy. However, these characterization methods take a long time, and they are based on only a small amount of large sample data for selection, and the data is very subjective and not rigorous[5]. In the above methods the pre-processed results are inaccurate due to improper operation. There are also some indirect measurement methods for CNF characterization, but the results are not satisfactory. For example, the light scattering method suitable for measuring the particle size distribution of spherical particles in the liquid is usually not suitable for CNF.

Therefore, we have used a dynamic characterization of cellulose nanofibrils, which can not only obtain the datum of a large number of samples, but also accurately measure the size of cellulose nanofibrils, and it is a non-contact characterization, and there will be no error due to improper operation.

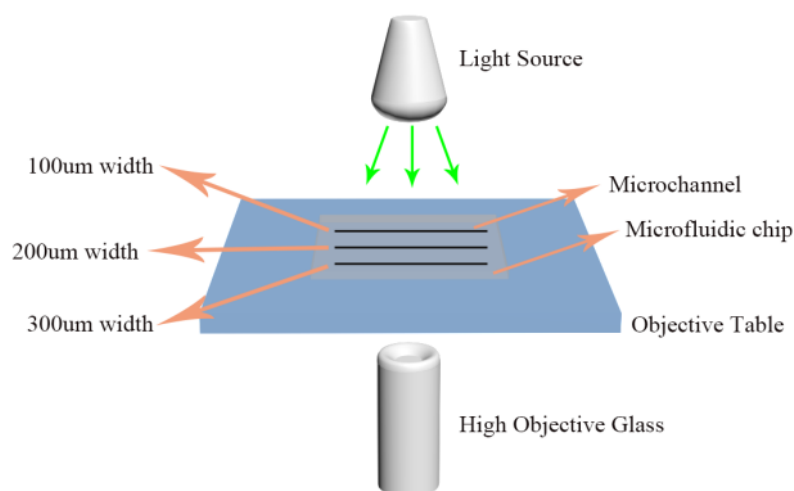
## 2. Preparation of Materials and Experiments

### 2.1. Materials and Experiment

The preparation of cellulose nanofibrils: The TEMPO/NaBr/NaClO system can selectively oxidize cellulosic alcohol hydroxyl groups in aqueous solution, and the oxidation of natural cellulose occurs on the surface of microfibrils. The carboxyl and aldehyde groups can be introduced without changing the morphology and crystallinity of the fibers. The CNF is obtained by the homogeneous treatment of the oxidized cellulose. [6]



The preparation of microfluidic chip: The chip is made of mold injection (mold with pure silicon) which is using PDMS material. PDMS material is injected into 3mm thickness and then bonded to 0.55 mm glass.



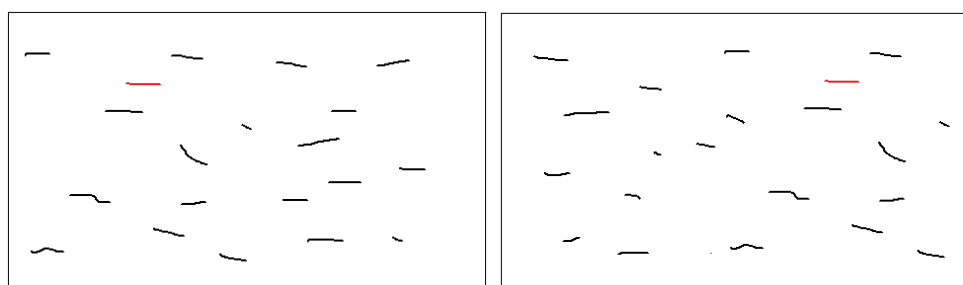
**Figure 1.** Schematic diagram of a test device

The schematic diagram of a test device is showed in the Fig.1. The suspension containing CNF was injected into the microchannel, and the injecting rate was 10nL/min. CNF particles in the microchannel are photographed by CCD(charge coupled device) camera, and then transfer the pictures captured by the CCD camera to the computer to handle the image.

## 2.2.The Principle of Measurement

**2.2.1.Optical principle.** The CNF in the microchannel is irradiated by the light source to produce a weak scattering light. After imaging on EMCCD (Electron-Multiplying charge coupled device camera), the outline of the nanofibers is different from the background. The center of the CNF is bright and the edge is dark. When CNF moves in the field of view (the whole detection area is 80um\*80um), there is a clear distinction between the particle and the background. It is easy to identify the moving CNF in video.

**2.2.2.The principle of velocity measurement.** Nanofibers are constantly moving in the flow field because of the influence of Brown movement, the morphology of nanofibers is constantly changing in the liquid.

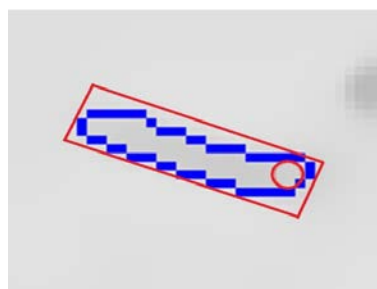


**Figure 2.** The labeled fiber after the identification of the flow field

In the Fig.2, the most similar nanofiber marked by red lines is found around a certain fiber image. In a certain range, the fiber is the only one. Thus, a single CNF in the flow field can be identified and the track of the motion is traced in a continuous multi frame image.

After identifying a specific CNF, the shift of the center point of the same fiber is analyzed in the two adjacent frames, and then the distance of the fiber moving at a specific time (each frame interval) is known, and the moving velocity of the particle can be calculated by  $V=X/t$ . The velocity of CNF particles can be obtained by continuous analysis of multiple frames.

**2.2.3. The principle of calculating size.** The nano fiber particles can be identified by the background difference. In the image, the outline of the nanofiber particles is outlined by the selected gray threshold. The size information is recorded by pixels.

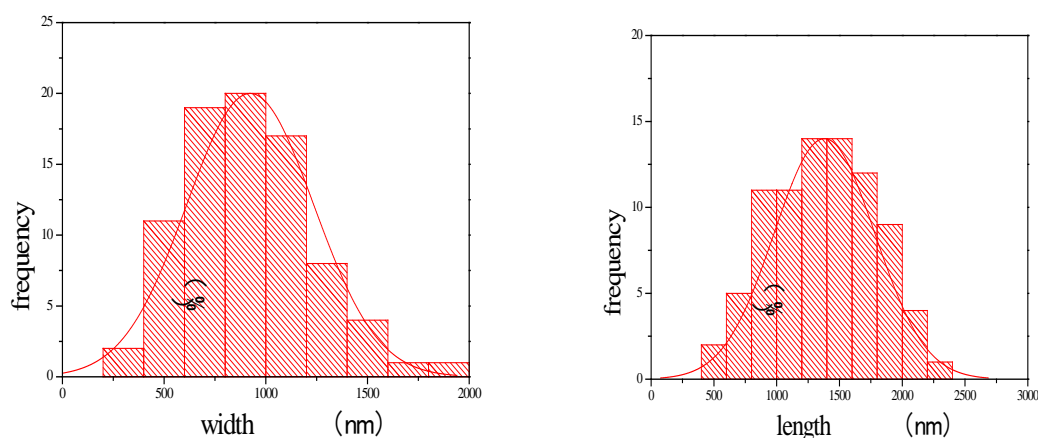


**Figure 3** The schedule of calculating the diameter and length of the fiber

In order to identify its diameter and length, a outer rectangular and inner circle is drawn on the contour of the fiber (draw a minimum rectangle around the fibrous image and draw the maximum inner circle in the fibrous image) in the Fig.3. The long side of the outer rectangle is the length of the fiber, the diameter of the inner circle is the diameter of the fiber, and the number of pixels occupied by the diameter and length can be magnified by microscope. According to magnification of microscope and resolution of CCD, it can be converted into actual length.

### 3. Results

There is a problem of limited resolution in the instrument because of some errors in the optimization of some images. This is caused by the limitations of the instrument itself, so we have studied the effect of the error of the instrument on the final data to correct the error by using a known size of gold nanoparticles (length of 300nm, 20nm width).



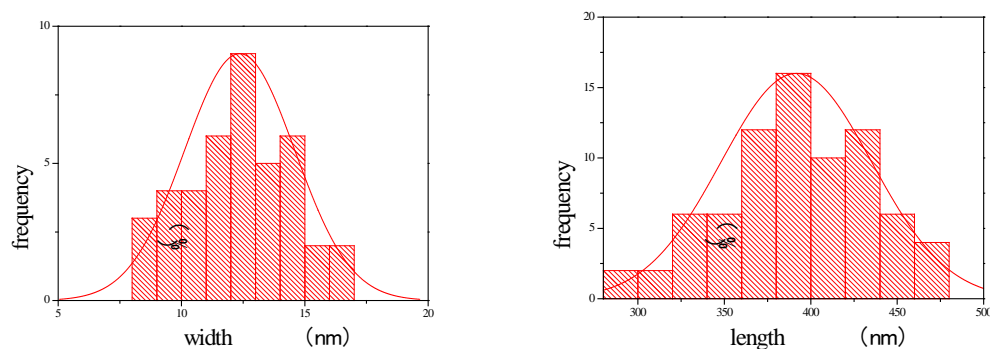
**Figure 4** The width and length distribution of gold nanoparticles after calculation

In the Fig.4, the center of the width of the normal distribution map is 900nm, the length of the normal distribution center is 1500nm. Therefore, it is necessary to multiply the correction actor for the ratio of actual size to measured data of gold nanoparticles in data analysis. The width value needs to be multiplied by  $1/45(20/900)$  in the analysis of the data, and the length value needs to be multiplied by  $1/5(300/1500)$  to get real and reliable data.

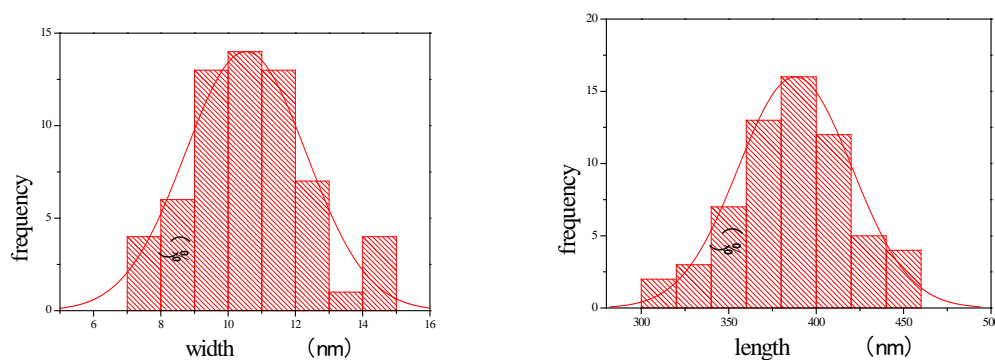


**Figure 5.** Morphology of nanoscale cellulose observed in flow channels of microfluidic chips

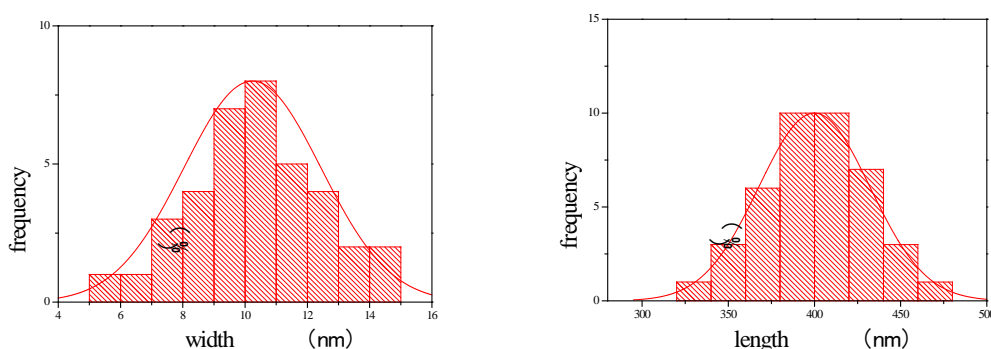
In the Fig.5, it can be seen clearly that the shape of CNF in the flow field is typical rod shape and keeps consistent with the flow direction. In the image, black is background and white is identified as nanocellulose. According to this image, the size of nanocellulose is analyzed.



**Figure 6 (a).** The statistical distribution map obtained by injecting 10nl/min into the 100um width channel.



**Figure 6 (b).** The statistical distribution map obtained by injecting 10nl/min into the 200um width channel.



**Figure 6 (c).** The statistical distribution map obtained by injecting 10nl/min into the 300um width channel.

The width in Fig.6(a) is mainly distributed in 12nm, the length is mainly distributed in 390nm, and the speed calculation is 327um/s. The width in Fig.6(b) is mainly distributed in 10.5nm, the length is mainly distributed in 390nm, and the speed calculation is 272um/s. The width in Fig.6(c) is mainly distributed in 10nm, the length is mainly distributed in 400nm, and the speed calculation is 223um/s.

From the above data, the length and width of this CNF sample are approximately the same, the width is about 11nm, the length is about 400nm, and the speed is different because the same flow of CNF suspension is injected into the channel of different width. The velocity of the suspension in the micro channel decreases with the increase of the width of the channel.

#### 4. Conclusion

The correct calculated data is gained by using nano gold particles with normal sizes. The size and the flow velocity of nanocellulose in the channel of microfluidic chip can be calculated by dynamic characterization. The velocity is different when the CNF suspension of the same flow is injected into different widths of microchannels. This new method is simple, convenient and suitable for the characterization of nanofibers.

#### References

- [1] Linsinger T, Roebben T, Gilliland D, Galzilai L, Rossi F, Gibson N and Klein C (2012): Requirements on measurements for the implementation of the European Commission definition of the term "nanomaterial". JRC Reference Reports, European Commission, Joint Research Centre (JRC), Institute for Reference Materials and Measurements, Brussels, Belgium.
- [2] De Azeredo H M. Nanocomposites for food packaging applications[J]. Food Research International, 2009, 42(9): 1240.
- [3] Favier V, Chanzy H, Cavaexe J. Polymer nanocomposites reinforced by cellulose whiskera[J]. Macromolecules, 1995, 28 (18): 6365.
- [4] Hamada H, Bousfield D W. Nanofibrillated cellulose ad a coating agent to improve print quality of synthetic fiber sheets[J]. TAPPI JOURNAL, 2010, 9 (11): 25.
- [5] Raposo M, Ferreira Q, Ribeiro P. A guide for atomic force microscopy analysis fo soft-condensed matter[J]. Modem Research and Educational Topics in Microscopy, 2007 (1): 758.
- [6] Qijun D, Jinsong Z, Bin W. Effect of retention rate of fluorescent cellulose nanofibrils on paper properties and structure. Carbohydrate Polymers, 2018, 186 (74).