Supporting Information

for Adv. Mater., DOI: 10.1002/adma.201704050

Anomalous-Diffusion-Assisted Brightness in White Cellulose Nanofibril Membranes

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Experimental details:

Materials: CNF is prepared from never dried birch pulp by disintegrating the pulp 6 times through a fluidizer (Microfluidics Corp., Newton, MA, USA) leaving a hydrogel with a consistency of approximately 1.5 wt. %. Ethanol (Etax Aa, > 99.7 vol. %) is purchased from Altia. 2-propanol and octane are purchased from Sigma-Aldrich.

Fractioning of the CNF dispersion by sequential centrifugation: The CNF gel is diluted to 0.3 wt. % by adding deionized water followed by vigorous stirring and homogenization with a high-shear homogenizer (Ultra Turrax T25 basic IKA Labortechnik) for 30 min at 11,000 rpm. After dilution and homogenization, the original CNF dispersion is centrifuged at 5,000 g-forces and the supernatant is collected. The CNF in this first fraction are called the “finest fibrils” in the text. Subsequently, the sediment is repeatedly diluted, redispersed and centrifuged again as described above, until the bluish hue resulting from scattering of light by the fine dispersed fibrils in the supernatant is no longer observed. Then, the same process is repeated with a lower centrifugal speed of 4,000 g-forces and the supernatant was again collected. The CNF in this second fraction are called the “medium fibrils” in the text. Lastly, after repeated dilution, homogenization, and centrifugation cycles the supernatant displays no bluish hue resulting from scattering of light, the sediment is collected, diluted and redispersed. The CNF in this last fraction are called the “coarsest fibrils” in the text. The sequential centrifugation process resulted in dispersions of varying transparency as illustrated in Figure 1b where the scattering is weakest for the first dispersion and strongest for the final one.
Preparation of porous CNF membranes: The porous membranes are prepared as previously described.[1] A given amount of one of the three fractioned CNF dispersions is vacuum filtered on a hydrophilic polyvinylidene fluoride filter membrane (0.45 μm, GVWP, Millipore) until a wet gel-cake is formed and no vibration of a water layer is observed when the filtering apparatus is sharply tapped. The filtration step is completed typically in 15 min. The filter and gel-cake are carefully transferred to a glass Petri dish and ethanol is pipetted to the edge of the filter paper before drying of the gel-cake occurred, while avoiding excessive mechanical disturbance to the gel-cake, until both are fully immersed in ethanol. After an approximate 5-minute soak in ethanol, the filter and gel-cake are inverted onto a smooth polytetrafluoroethylene (PTFE) sheet leaving the gel-cake resting on the PTFE and the filter membrane on top. A small amount of ethanol is pipetted on the gel-cake to avoid drying and the filter membrane is carefully peeled from the gel-cake and discarded. The gel-cake is covered with 2-propanol for typically 5 min to exchange the remaining water and ethanol in the gel-cake to 2-propanol after which the used 2-propanol is discarded and new is added. This is repeated three times. After solvent exchange to 2-propanol, the same procedure is repeated using octane. After the gel-cake is soaked three times in octane, the excess octane is discarded and the gel-cake is left to dry slowly on the PTFE sheet in ambient conditions while partially covered with a glass Petri dish. During all soaking steps, the gel-cake and solvent are covered with an upside-down Petri dish to avoid drying.

Preparation of dense and compact CNF films: Compact CNF films, as opposed to porous membranes, are prepared similarly to the membranes but, after peeling of the filter membrane,
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the solvent is exchanged back to water. In this case the gel-cake is dried slowly from water on the PTFE sheet.

**Thickness measurement:** The thicknesses of the films are measured with a film thickness measurement set-up composed of a displacement sensor (LGF-0110L-B, Mitutoyo), digital reader (EH-10P, Mitutoyo) and a measuring table with support for sensor (215-514 comparator stand, Mitutoyo).

**AFM characterization of the fractioned CNF:** The morphologies of the fractioned CNFs are investigated using a Dimension 5000 scanning probe microscope with NanoScope V controller (Veeco). The samples are prepared by first diluting a dispersion of the fractioned CNF to approximately 0.001 wt. % with deionized water and pipetted onto a clean microscope glass slide. The excess dispersion is removed by turning the glass slide vertical. Subsequently, the samples are dried at room temperature for 24 h prior to measurement. The images were scanned in tapping mode in air using silicon cantilevers (NSC15/AIBS) provided by MicroMash (Tallinn, Estonia). The data is post-processed in order to flatten the substrate background and remove streaks from scanning artefacts.

**SEM characterization:** Dry porous CNF membranes are imaged with SEM from the top- and from the cross-sectional view. For the top-view, small pieces of membranes are cut and attached to an aluminum SEM stub with carbon tape. An approximately 4 nm thick gold film is sputtered (Emitech K100X) on the samples. Imaging is carried out with a Zeiss Sigma VP scanning electron microscope at 1-2 kV acceleration voltage.

**Exposure of non-fracture cross-section of membranes by cryo-microtoming:** Narrow strips of dry CNF membranes are glued at one end to an aluminum stub with epoxy while leaving the other end pristine. The attached samples are briefly soaked in cyclohexane, which is subsequently quickly frozen in liquid nitrogen. After freezing, the samples are transferred to a
Leica 125 Ultracut microtome that has been pre-cooled to -150 °C. The cross-sections of the samples are first cut flat with a trimming knife, and subsequently a smooth surface for imaging is exposed with a diamond knife. After microtoming, the samples are transferred to a vacuum oven while under liquid nitrogen and supported by a massive, pre-cooled metal block, and the cyclohexane is sublimated out from the samples at reduced pressure overnight. The vacuum dried samples are sputtered and imaged with SEM as described above.

*Estimation of pore size distribution from SEM micrographs of cross-sections of membranes:* The cross-sections of membranes were exposed and imaged as described above. The pore size distribution was estimated with automated image analysis using ImageJ 1.51s. All SEM micrographs analyzed were taken with 20,000 x magnification, and four to five micrographs were analyzed of each membrane. The scale was calibrated by measuring the length of the scale bar generated by the SEM software and setting the corresponding pixel-to-distance ratio as a global calibration. Subsequently, the images without the imaging data panel were converted to binary images by selecting an intensity threshold above which all pixels were set to zeros, and all below the threshold were ones. The threshold was selected manually and separately for each micrograph. The binary images were analyzed using the Analyze Particles algorithm with circularity ranging from 0.0 to 1.0 and the particle area threshold ranging from 0 to infinity. The values used from the analysis were the lengths of the major and minor axes of the ellipse fitted over each pore. The number of pores sampled for the transparent, the semi-transparent, and the white membranes were 9558, 15539, 5785, respectively.

*Specific surface area and pore size distribution by nitrogen adsorption:* N₂ physisorption data are measured at least once for each of three identically prepared CNF membranes with a Micromeritics TriStar II automated system. The samples, 10-20 mg each, are stabilized for 1 h under vacuum in their measurement vessels before adjusting the transducers to zero and
running free-space measurements with helium both at ambient and measurement temperature (77 K). The adsorption isotherm is collected for nitrogen by increasing the relative pressure from 0 to 0.99 and back while recording over 100 data points. The Brunauer-Emmett-Teller specific surface area analysis\(^2\) (BET) is carried out for a relative \(N_2\) vapor pressure of 0.05 – 0.30. Pore size distribution is determined according to Barrett-Joyner-Halenda (BJH) method\(^3\) from the full adsorption isotherm range. This method assumes an ideal cylindrical pore shape.

*Total transmittance and reflectance measurements:* The samples are illuminated using a Xenon lamp Ocean Optics HPX-2000 coupled into an optical fiber (Thorlabs FC-UV100-2-SR). The transmitted/reflected light is collected by an integrating sphere (Labsphere) and the signal is acquired by a spectrometer (Avantes HS2048). The integrating time is set to 1 s and 10 spectra are acquired for each sample of different thickness and averaged together.

*Angular resolved measurement:* The angular distribution of scattered/transmitted light is determined using a goniometer setup. The samples are illuminated using a Xenon lamp Ocean Optics HPX-2000 coupled into an optical fiber (Thorlabs FC-UV100-2-SR). The illumination angle is fixed at normal incidence and the angular distribution of intensity acquired moving the detector arm with a resolution of 1°. An interval of 180° around the normal incidence direction has been acquired. The detector used for this setup is a 600 μm core fiber (Thorlabs FC-UV600-2-SR) connected to a spectrometer (Avantes HS2048). The spectra are acquired with an integrating time of 0.2 s and averaged over 10 acquisitions. To filter out the reflection from the sample-air interface, the scattered intensity is acquired between crossed polarizers (Thorlabs WP25L-UB). This polarization configuration does not affect the sample response as the multiple scattering within the sample randomizes the incoming polarization. Due to the imperfect extinction of the polarizers, a small percentage of the light reflected at the sample...
interface reaches the detector. This small contribution does not influence the measurements for the white and semi-transparent membranes but does not allow to reliably acquire the reflected distribution for the transparent ones. For this reason, the data for the transparent membranes are not reported in Figure S7. The experimental data have been normalized against a standard white diffuser (Labsphere SRS-99-010) or their maxima for the scattering and transmission measurements respectively.

*Speckle measurements and analysis:* The samples are illuminated from the front with a collimated laser beam (NKT SuperK EXTREME tuned to central wavelength 635 nm with a SuperK VARIA) and the image of the output speckled pattern is recorded by a charged-coupled-device camera (IDS UI-3580LE). The sample is placed on a motorized stage (Thorlabs Z825B) so that each image is collected for a different location on the sample (i.e. the sample is moved by a distance greater than the illumination spot, 400 µm in diameter. More than 2000 images are acquired for each sample). The sample is mounted between crossed polarizers (Thorlabs LPVISE100-A; transmittance at 600 nm = 80%) in order to extinguish any residual ballistic light (see Figure S12). Filter paper (Whatman® filter paper, Grade 1) is used to compare the samples to a standard diffusive material. Examples of the images obtained are shown in Figure S13.

The images obtained with this method are then analyzed in ImageJ in order to extract the intensity profile across the diameter of the speckle pattern. In other words, the gray levels of the images across a line through the middle of the speckle are recorded as a function of position. From these intensity profiles, their full width at half maximum (FWHM) of the intensity is computed. The FWHM values of each speckle pattern are normalized with respect to the average FWHM. Finally, to illustrate the variation in speckle shapes, a histogram of the normalized FWHMs is generated using a MATLAB script. Similarly, the maximum intensity
of each image is normalized to the image’s total intensity and the probability density is plotted in MATLAB.

As the thickness of the CNF membrane is much smaller (~10 times) than that of the filter paper, the average image intensity of the first is always greater than the latter one. Therefore, the histograms are renormalized in order to plot the two populations on the same scale. Furthermore, the correlation between the maximum intensity of each speckle and its FWHM radius is analyzed, as shown in Figure S14.
Figure S1. AFM micrographs of (a,b,c) finest, (d,e) medium, and (f,g) coarsest fibrils.
Figure S2. Fiber diameter histograms and fitted log-normal models of (a) finest, (b) medium, and (c) coarsest fibrils. Note that both the horizontal and vertical axes in (c) are different from those of (a) and (b). A comparison of the fitted log-normal models is shown in (d) with the vertical axis as logarithmic to highlight the presence of a small amount of significantly thicker fibrils. Parameters for fitted models can be found in Table S1.
Table S1. Parameters describing log-normal models fitted to AFM thickness data of each CNF fraction. The parameters $\mu$ and $\sigma$ refer to the parameters of the log-normal probability density function which is of the form: $P(x) = \frac{1}{x\sigma\sqrt{2\pi}}e^{-(\ln(x) - \mu)^2/2\sigma^2}$.

| Parameters | Finest fibrils diameter [nm] | Medium fibrils diameter [nm] | Coarsest fibrils diameter [nm] |
|------------|------------------------------|-----------------------------|-------------------------------|
| Mean       | 4.2                          | 5.6                         | 19.5                          |
| Standard deviation | 2.7                          | 3.2                         | 13.2                          |
| $\mu$      | 1.26                         | 1.57                        | 2.78                          |
| $\mu$-95 % confidence interval | (1.21, 1.31) | (1.52, 1.62) | (2.73, 2.83) |
| $\sigma$   | 0.59                         | 0.54                        | 0.61                          |
| $\sigma$-95 % confidence interval | (0.56, 0.63) | (0.51, 0.57) | (0.58, 0.65) |

Figure S3. The pore width distribution of the porous membranes investigated by nitrogen physisorption. Note that the calculation method of the pore diameters assumes cylindrical pores, which does not hold for the present materials. Only every 7th data point is shown.
**Figure S4.** Examples of SEM micrographs of cross-sections of (a,b) transparent, (c,d) semi-transparent, and (e,f) white membranes used for estimating the pore size distribution of large pores with automatic image analysis using ImageJ. The cross-sections were exposed by cryomicrotoming in frozen cyclohexane followed by freeze-drying. The areas highlighted with the red color are the pores recognized by the algorithm. The histograms of the pore widths and heights are shown in **Figure S5**.
Figure S5. Histograms of estimated frequencies of pore sizes from SEM micrographs (see examples in Figure S4) of cross-sections of (a) transparent, (b) semi-transparent, and (c) white membranes. The analysis was carried out with ImageJ. Major and minor pore axes refer to the axes of the ellipse fitted over each pore in the algorithm. In essence, the major axis refers to length of the larger dimension of the pore, while the minor axis refers to the smaller. The number of pores sampled for the transparent, the semi-transparent, and the white membranes were 9558, 15539, 5785, respectively.
Figure S6. Total reflectance spectra for (a) transparent, (b) semi-transparent, and (c) white membranes for different membrane thicknesses as compared to common filter paper (dashed red line). The response for filter paper is rather flat over all wavelengths while the membranes tend to scatter more efficiently the shorter wavelengths. This agrees with the numerical calculations in Figure S10. The fact that blue wavelengths are reflected more strongly can be considered advantageous as typically short-wavelength brightening agents have to be added to common paper to enhance such spectral range in order to enhance the whiteness of paper to the human eye.
Figure S7. Polar plot of the angular distribution of reflected light at 400 nm. Two samples of similar thickness (about 8 µm) but different fabrication protocols are compared. The white membrane, blue markers, reflects more than twice the amount of light of the semi-transparent one, green markers. Both samples show an intensity distribution close to the Lambertian one for ideal diffuser (represented in the graph by the solid lines).

To prove that the semi-transparent and white membranes would not be appropriately described by normal diffusion, we compare the fits for normal diffusion and Ohm’s law (which accounts for both the absorption length $l_A$ and for the extrapolation length $z_e$) with those for anomalous diffusion, Figure S8. The expressions used are, for normal diffusion\textsuperscript{[5]}

$$T = \frac{1}{1 + AL^*},$$  \hspace{1cm} \text{(S1)}

and, for Ohm’s law\textsuperscript{[6]}

$$T = \frac{\cosh \frac{z_e}{l_A} \sinh \frac{5z_e}{3l_A}}{\sinh \frac{L + 2z_e}{l_A}},$$ \hspace{1cm} \text{(S2)}

where $T$ is the total transmittance and $L$ is the thickness of the sample. Table S2 and Table S3 summarizes the parameters inferred from the fitting routine.
**Table S2.** Parameters used for the normal diffusion fitting.

| Membrane appearance | Parameter A [µm⁻¹] | Standard deviation in A [µm⁻¹] |
|---------------------|---------------------|-------------------------------|
| Transparent         | 0.004               | 0.0005                        |
| Semi-transparent    | 0.050               | 0.006                         |
| White               | 0.231               | 0.035                         |

**Table S3.** Parameters used for Ohm’s law fitting.

| Membrane appearance | Absorption length lₐ | Standard deviation in lₐ | Extrapolation length zₑ | Standard deviation in zₑ |
|---------------------|-----------------------|--------------------------|-------------------------|--------------------------|
| Transparent         | 262.6                 | 26.9                     | 214.1                   | 21.9                     |
| Semi-transparent    | 37.2                  | 7.6                      | 30.3                    | 6.2                      |
| White               | 6.7                   | 3.1                      | 5.4                     | 2.5                      |

**Figure S8.** Fit of the data using two alternative approaches - Ohm’s law (in blue) and the normal diffusion equation (in red) – as compared to the fit from normal diffusion (in black). Whilst for the transparent membranes no obvious difference is noticeable, for the semi-transparent, and white membranes the alternative fits are clearly unsatisfactory.
Figure S9. SEM micrographs of cryo-microtomed cross-sections of (a) transparent, (b) semi-transparent, and (c) white membranes. For cryo-microtoming at -150 °C the samples are soaked in cyclohexane at room temperature, which is subsequently quickly frozen in liquid nitrogen. After cryo-microtoming the frozen cyclohexane is sublimated in a vacuum oven. The micrographs support the claim that while the fibrils (and consequently flat voids) are mostly oriented in-plane, no distinct pseudo-layers are present.
Investigation of the role birefringence

As CNFs have been reported to be birefringent, it can be speculated that the light propagation is affected by the difference in the refractive index. However, Mie scattering simulations show that the difference does not significantly affect the scattering efficiency $Q_{sca}$, see Figure S10. This is confirmed by the speckle statistics if the sample is placed between polarizers, so that the s- and p-polarizations can be measured separately (Figure S11). The experimental set-up is analogous to the one for the speckle measurements but the two polarizers are rotated with respect to each other by ±90° to measure different polarization channels.
Figure S10. Scattering efficiency as a function of wavelength for cellulose spheres in air (top) and air spheres in cellulose (bottom). As expected, particles with diameters around 200-500 nm are stronger scatterers. Interestingly, the scattering strength for the air inclusions is similar to the one of cellulose spheres. Calculations performed using MiePlot by Philip Lavern.
Figure S11. The speckle statistics for the super-diffusive sample are the same for s- and p-polarisation (see legend) implying that the birefringence of the fibers does not affect the light transport.

Figure S12. The experimental set-up used to perform the speckle measurements. P₁ and P₂ are two polarizers in crossed configuration. Lens L₁ to resize the speckle pattern to fit the sensor of the charged-coupled-device (CCD).
Figure S13. The speckle patterns obtained clearly show that common filter paper (A) and the white CNF membranes (B) give rise to a scattered intensity cloud while the transmission through (C) the semi-transparent, and (D) the transparent samples, with a more homogenous microstructure, is mostly ballistic. It is interesting to note that the speckle size is greater for the CNF membranes than for the paper: this can be caused by the scatterers being larger in size and/or the optical thickness being greater for paper.[4]
Figure S14. The relative maximum intensity vs. the relative FWHM of each speckle pattern. The intensity of the speckle patterns and their radii are correlated. As expected, the higher maximum intensities are observed for the smaller speckle radii.

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