Water-Induced Structural Rearrangements on the Nanoscale in Ultrathin Nanocellulose Films

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Abstract

Many nanoscale biopolymer building blocks with defect-free molecular structure and exceptional mechanical properties have the potential to surpass the performance of existing fossil-based materials with respect to barrier properties, load-bearing substrates for advanced functionalities as well as light-weight construction. Comprehension and control of performance variations of macroscopic biopolymer materials caused by humidity driven structural changes at the nanoscale are imperative and challenging. A long-lasting challenge is the interaction with water molecules causing reversible changes in the intrinsic molecular structures that adversely affects the macroscale performance. Using in situ advanced X-ray and neutron scattering techniques, we reveal the structural rearrangements at the nanoscale in ultrathin nanocellulose films with humidity variations. These reversible rearrangements are then correlated with wettability that can be tuned. The results and methodology have general implications not only on the performance of cellulose-based materials, but also for hierarchical materials fabricated with other organic and inorganic moisture sensitive building blocks.

Introduction

One-dimensional nanoparticles such as nanofibers, nanowires or nanorods attract increasing attention due to their physical properties given by their high-aspect ratio.¹ Cellulose nanofibers (CNF) are very attractive due to their earth abundant bio-based origin and biocompatibility, having favorable properties such as lightweight, thermal stability, and good mechanical strength.²⁻⁴ These attributes make CNF a very promising precursor for the design of high-performance bioinspired materials and nanocomposites.⁵⁻⁶ Drawbacks for bio-based materials are still systematic control of quality, influence of solvent absorption and limited life-time, compared to some fossil-based materials. However, keeping in mind the
growing environmental concerns, CNFs are already finding their way to a wide range of applications from transparent conductive nanopaper to ultra-strong bio-active fibers.\textsuperscript{7–10} Over the last decades sustainable materials have also gained increasing attention for future flexible, biodegradable, yet disposable electronics.\textsuperscript{11–14} Transparent cellulose nanopaper is used already in small devices due to its mechanically strength, flexibility and conformability originated from the CNFs nanosize and soft nature. The CNFs also yield a smoother nanopaper compared to paper made from conventional cellulose fibers.\textsuperscript{13} In such applications surface roughness and porosity is an important factor that affects the device compatibility, as high surface roughness may lead to inhomogeneities and a decrease in performance for thin film based applications as optoelectronic devices.\textsuperscript{15–18} Industrial-style airbrush spray deposition facilitates scalable roll-to-roll (R2R) compatible and transferable technology with high acceptance in the coating area, such as for sprayed flexible organic photodiodes,\textsuperscript{19–23} being widely applied in edible coatings consisting of sprayed cellulose on fresh or processed food to prevent mold. Such coating can also act as a partial barrier to moisture as well as to improve handling properties.\textsuperscript{24} Tailoring of the hygroscopic behavior affecting the wettability of the material, which would provide means for reducing physical degradation, e.g. as swelling and loss in mechanical strength. This has been shown by Li et al. who tuned wettability by incorporating polyurethane acrylate.\textsuperscript{25}

In this work, we have investigated nanoscale morphological rearrangements in spray deposited low-roughness hydrophilic ultrathin CNF films having unprecedented low roughness and switchable, tailored wettability. Atomic force microscopy (AFM) as well as optical microscopy was used to quantify the differences in the surface topography. Grazing incidence small-angle X-ray and neutron scattering (GISAXS / GISANS) are surface sensitive scattering techniques with statistical relevance\textsuperscript{26,27} and were employed to study the morphological features within the ultra-smooth CNF thin films under as prepared conditions as well as their rearrangement under humidification. Contact angle measurements were conducted to resolve the surface free energy of the nanocellulose thin films fabricated with different surface
charge densities of CNFs.

**Experimental Section**

**Sample preparation.**

CNFs were prepared from chemically bleached wood fibers (60% Norwegian spruce and 40% Scots pine, Domsjo AB, Sweden). The wood pulp fibers were chemically treated with a 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO)-mediated oxidation reaction. In order to obtain CNFs with different surface charge densities (400, 800, 1000, 1360 µmol/g), we followed a protocol described elsewhere. The gel like suspensions were diluted by adding ultrapure water, mixed thoroughly using a mechanical mixer (12000 rpm for 10 min, Ultra Turrax, IKA, Germany) and sonication (10 min, Sonics Vibra-Cell CV33, USA). The diluted suspensions were then centrifuged (Rotina 420, Hettich GmbH & Co. KG, Germany) at 5000 rpm for 60 minutes. The dry content of the suspensions was determined by gravimetric analysis and adjusted to 0.07 wt%. The resulting suspension was then used for the airbrush spray deposition experiments. The average length of CNFs is around 500 nm and the diameter is around 2.5 nm.

As substrate, polished silicon (Si) wafers (Si-Mat, Germany) were used. The wafers were cut to (20 × 20) mm² for GISAXS measurements and (20 × 100) mm² for GISANS measurements. The wafers were first cleaned with solvents (ethanol, acetone, isopropanol, all Carl Roth, Germany) and subsequently cleaned with ultrapure water (Milli-Q, 18.2 MΩcm⁻¹), followed by an acid bath (87.5 mL hydrogen peroxide 30%, 190 mL sulfuric acid 96%, 37.5 mL ultrapure water, all Carl Roth, Germany) at 80°C for 15 min. This procedure yields a superhydrophilic sample surface. All used chemicals are listed in the SI.
Airbrush spray deposition.

The spray deposition experiments were performed by facilitating an airbrush spray device (Compact JAU D555000, Spray Systems, Germany) at the beamline P03 (see Figure 1). The CNF suspension was supplied by a siphon attached to the airbrush spray device.

![Figure 1: Schematic of the spray setup used at the synchrotron beamline P03 at DESY. In situ spray deposition is performed while analysing the layering process with GISAXS.](image-url)

The spray deposition was achieved through atomization of the CNF suspension with compressed nitrogen at a gas pressure of 1 bar. The nozzle-to-substrate distance of 200 mm led to spraying in the very dilute regime (see Lefebvre et al.\textsuperscript{30}). We used a spray protocol as following, 0.5 s spraying, 2 s waiting, in 20 cycles, corresponding to a film thickness $x \approx 200$ nm. Ohm et al.\textsuperscript{31} showed that the film thickness linear increase with the used number of spray pulses when intermittent drying is used. The Si substrate temperature was controlled to 100 °C. This protocol and the heated surface caused the films to dry evenly suppressing visually, by the use of a microscope, any coffee-ring effects as previously shown for nanoparticles.\textsuperscript{32–34} The GISANS samples were prepared using CNF with 1000 µmol/g and the same above mentioned protocol but with larger Si substrates (20 × 100) mm. To cover the full wafer, the spray nozzle was cyclic translated 150 mm with 30 mm/s and 75 spray pulses with the above mentioned conditions; 0.5 s spraying and 2 s waiting. This yielded the same surface roughness and thickness as the above mentioned smaller samples proving the
scalability of our approach.

**Atomic force microscopy.**

The AFM measurements were conducted using a MultiMode (MMAFM-2, Bruker Corporation, USA) AFM with a silicon nitride based cantilever for soft materials (Scanasyt-AIR-HR, resonance frequency: 130 kHz, spring constant: 0.4 N/m, Bruker Corporation, USA) with a nominal tip radius of 2 nm. The ScanAsyst mode, a tapping mode, was used to map the AFM topographical maps. The rms roughness was analysed from the AFM topographical maps (10 × 10) µm². Therefore, five measurements were performed on different positions of the sample and averaged. The thin film thickness was analyzed by scratching the CNF sample surface in the middle of the wafer. (see Figure S1 and Table S1).

**Surface sensitive X-ray scattering.**

The GISAXS experiments were conducted at the P03 beamline at the PETRA III synchrotron at DESY (Hamburg, Germany), using a sample-to-detector distance, SDD = (5007 ± 1) mm with an incident photon energy of \( h\nu = 13 \text{ keV} \) (\( \lambda = 0.9537 \text{ Å} \)) and a beam size of (H × V, 16 × 22) µm². In order to observe the complete scattering pattern a 2D pixel detector PILATUS 1M (Dectris Ltd., Switzerland) was used, with a pixel size of (172 × 172) µm² and (981 × 1043) pixels² for the GISAXS measurements. The high-resolution GISAXS measurements were conducted at the same geometry with a 2D pixel detector Lambda 750K (X-Spectrum, Germany) with a pixel size of (55 × 55) µm² and (512 × 1536) pixels². The X-ray angle of incidence was set to \( \alpha_i = (0.41 ± 0.01)° \) in order to penetrate the whole film thickness. Each GISAXS pattern was exposed for 0.5 s and a lateral scanning step size of 100 µm was used for avoiding radiation damage (see Figure S2-S3). 1D intensity distributions were extracted from the 2D GISAXS pattern (see Figure S4) using the DPDAK software package and later fitted using minimum chi-square estimation with a cylindrical form factor as previously introduced by Schaffer et al.\(^{37–39}\)
Surface Sensitive Neutron Scattering

The GISANS experiments were conducted at the KWS-1 instrument operated by the Jülich Centre for Neutron Science (JCNS) at the research reactor FRM II at the Heinz Maier-Leibnitz Zentrum (Garching, Germany).\(^\text{40,41}\) A sample-to-detector distance, \text{SDD} = 3.7\text{ m} was used with an incident neutron wavelength of \(\lambda = 5\text{ Å}\) with using a 10\% wavelength selector and a beam size of \((10 \times 1)\text{ mm}^2\). The detector was a two-dimensional Li-scintillation anger camera with a pixel size of \((5 \times 5)\text{ mm}^2\) and \((112 \times 112)\) pixels\(^2\). The neutron incidence angle was set to \(\alpha_i = (1 \pm 0.01)^\circ\). Acquisition time for each GISANS pattern was 2\text{ h}. Analogous data treatment procedures were done as explained in the GISAXS part. For the GISANS experiments a humidity controlled (0\% to 90\% RH) sample chamber was used. Changes between humidity to equilibrium takes up to 20\text{ min}; another hour was waited prior to the individual measurements to ensure full hydration or drying.

Contact Angle Measurements

Sessile-drop contact angle measurements were made to monitor the wettability on the different charged cellulose thin films, using an OCA20 (Data Physics, Germany) contact angle measurement system. The volume of the drops were controlled with an automatic syringe system to 1\text{ µL}. To calculate the free surface energy within the Owens, Wendt, Rabel and Kaelble (OWKR)\(^\text{42}\) method three different polar and unpolar solvents were used, starting with ultrapure water (Milli-Q, 18.2 M\(\Omega\text{ cm}^{-1}\)), ethylene glycol (\(> 98\%\), Carl Roth, Germany), diiodomethane (\(\geq 99.4\%\), VWR, USA). The polar and dispersive components can be found in Table S2. Five droplets for each solvent were placed and the contact angle on both sides from each measurements were averaged for the surface free energy calculations later on. The contact angles are shown exemplary for the four different charge densities in the Figure S5. All calculation were done within the software SCA20 (Data Physics, Germany).
Results and Discussion

Topographical Information

The AFM images show a smooth, closely packed thin film (Figure 2 a - d). Dai et al. successfully showed the use of cellulose nanopaper as dielectric material for low-voltage field-effect transistors. The transistor is fully functional even under bending, which underlines the good-networking properties while staying flexible.\(^9\) Thin films flexibility and toughness can only be achieved if the film forms a densely packed network with little defects. The advantage when using spray deposition is that we could tailor the thickness while retaining the densely packed CNF network. No observable difference in the appearance of the influence of the different surface charges are noticed from the AFM mapping. For all cases, the nanofibers are well distributed into a web structure without obvious agglomeration or large-scale domains. By resolving individual fibers, one can study the alignment over the sample area and we can not observe any preferential alignment from the center to the outer regions of the thin film caused by the spray conditions. The thin CNF film is very homogeneous in fibril distribution without variation towards the outer regions of the spray cone. The film thickness of all samples is constant (191±5 nm) (Table S1). However, the optical microscope images for all four cases in Figure 2 show larger entities as brighter spots, which stem from bigger agglomerates of CNFs.

The radial power spectral density (PSD) is fitted using a cylindrical form factor approximation with paracrystalline order (see Figure S6 and Table S3), which visualizes the morphological changes on the surface due to the radially disordered morphology on the surface topography (see Figure S7).\(^{38}\) In the region below 0.008 nm\(^{-1}\), slight differences between the films can be observed, which may be attributed to structures at the resolution of power spectral density distribution. Within the resolved scales one finds medium-sized structures on the surface with a radius of \(r_{AFM} = (26.7\pm0.5)\) nm in a distance of \(d_{AFM} = (69\pm16)\) nm to each other, which do not change with surface charge.
Figure 2: AFM topographic images with four different surface charges, (a) 400 µmol/g, (b) 800 µmol/g, (c) 1000 µmol/g, (d) 1360 µmol/g. The insets are optical microscopy images of the corresponding films.
Figure 3: Root-mean-square (rms) in nanometer of the roughness (black, blue) and the water contact angle (red) of the different charged cellulose thin films. The trend of the roughness is linearly fitted for better visualization (dashed line). The blue diamond is a comparison to spray deposited enzymatic CNFs with similar thickness.\textsuperscript{31}
Figure 3 presents the root-mean-square (rms) roughness of the fabricated thin films plotted for the four different surface charges and compared to our previous results for sprayed enzymatic cellulose thin films.\textsuperscript{31} The graph shows that the surface roughness of the thin films decreases following a linear decay with increasing surface charge of the CNFs, see Eq. 1 in SI. The graph includes also the contact angle of water as function of surface charge. The contact angle decreases linearly when changing surface from \( \approx 27^\circ \) to \( \approx 14^\circ \) from 400\,µmol/g to 1000\,µmol/g respectively. This feature can be attributed to the decreased surface roughness. When the roughness decreases even more the contact angle, however, raises up to \( \approx 22^\circ \), which we speculate is driven by the increased ionic strength. Ahola et al. and Qi et al.\textsuperscript{43,44} showed that for spin-coated layer-by-layer fabricated thin films the roughness depends on the charge, from 4\,nm for low surface charge to 2 – 3\,nm with high surface charge. They also found that low charged CNFs do not form a densely packed thin film but rather a loose network. Sprayed CNFs made of enzymatic cellulose shows a surface roughness of around \((23 \pm 1)\,\text{nm}\) when prepared under similar conditions, having a surface charge of around 50\,µmol/g.\textsuperscript{45} This corresponds to the difficulties in the fibrillation process of enzymatic CNF which typically results in agglomerates, compared to the well dispersed fibers in the case of highly charged TEMPO-CNF. In the present experiments, the lowest roughness of \((2.5 \pm 0.6)\,\text{nm}\) was found for the highest surface charge \((1360\,\text{µmol/g})\) on a large-scale of \(20 \times 100\,\text{mm}\). Here, we assumed the highest roughness due to repulsion of the single fibers from each other, which clearly does not seem to be the case. This may instead be attributed to an ordering effect via repulsion. Benselfelt et al. found in a drop-casted self-assembly study of CNF on a substrate no obvious correlation between roughness and higher surface charges.\textsuperscript{46} Felix et al. confirmed stratification in spray deposited multilayer thin films using neutron reflectometry.\textsuperscript{47} They tuned the distance between layers and could thereby prove a super-lattice structure. We assume that the additional surface charge of the CNF used in our investigations allows for a improved smoothening. We deduce that the layering process is improved when intermittent drying in between single spray pulses.
occur as earlier described for enzymatic CNF by Ohm et al.\textsuperscript{31} and for polystyrene colloids by Zhang et al.\textsuperscript{32} The increased surface temperature during spray deposition results in a fast solvent evaporation which inhibits the aggregation of nanocolloids and yield smooth monolayers, as shown previously by Zhang et al.\textsuperscript{32} During spraying we deposit small droplets of CNF suspension on the heated substrate, the droplets coalesce and dry. The resulting thin film thus consists of many coalesced droplets, due to increased temperature the small droplets do not form any type of visual coffee-ring effect. Apparently, the highest surface charge promotes nanofiber assembly in such a way that nanoscale building blocks form a uniform and homogeneous densely packed film with unprecedented low roughness compared to typical spray deposited thin films. This demonstrates that the surface roughness of spray deposited thin films can be tuned by varying surface charge density of the building blocks.\textsuperscript{19} Nordenström et al. argued that increasing surface charge density of the CNF suspensions promotes an electrostatic stabilisation of the system, which is a beneficial aspect for the non-agglomerating self-assembly of the films.\textsuperscript{48} While the water evaporation caused a rapid increase of the CNF suspension causing increased ionic strength leading to gel formation, followed by an immediate lock-in, which we hypothesize is the driving force for the smoothing of our spray deposited thin films.

**Thin film morphology**

In order to investigate the inner morphology of the spray deposited CNF thin films, GISAXS measurements were performed on all samples, providing a possibility to probe all relevant length scales from nano- to microscale, which is beneficial for characterising the layering process.\textsuperscript{27} Due to the penetration depth of GISAXS, one obtains information on both the surface morphology and the self-assembly within the thin film. Figure S8 a - d depicts the 2D GISAXS pattern of the four different CNF films. The inset show a high resolution
zoom-in of the region around the critical angle of the materials (Yoneda region, see SI for details). The angle of incidence \( \alpha_{in} = (0.41 \pm 0.01)^\circ \) is well above the critical angle \( \alpha_{crit,CNF} = (0.13 \pm 0.01)^\circ \), and accordingly the whole film thickness is probed. The value found for the critical angle is in good agreement with the theoretical value for cellulose of \( \alpha_{crit,cellulose} = 0.12^\circ \), the deviation of \( \alpha_{crit,\Delta} = 0.01^\circ \) can be attributed to the nano-sized structured fibers in comparison to bulk cellulose.

Two distinct line cuts (see SI) were performed on the GISAXS pattern, a horizontal integration in \( q_z \)-direction and a vertical integration in \( q_y \)-direction, respectively shown in Figure 4 (a) and (b) (details see Figure S4). From these two line cuts, one is able to deduce the thin film morphology parallel and vertical to the surface. The one-dimensional intensity distribution along \( q_y \) is fitted with a model using upright standing cylinders with a radius \( r_i \) and a distance from center-to-center of \( d_i \) similar to the PSD fitting. This is the best approximation of scattering centers for the scattered intensity, for details see inset Figure 4 (a). The index \( i = 1, 2 \) shows the values for two-domain feature sizes which we found in the film morphology. This model represents a projection of the internal structure of the film onto the surface, i.e. it is directly coupled to the two-dimensional representation of the models used for evaluating the scattering results. This approximation provides a tool to be used on complementary methods as AFM, GISAXS and GISANS. The fit results are shown in Table S4. Two characteristic structural entities have been found in the film, which we attribute to the agglomeration of CNFs, the larger with \( r_1 \approx 27 \) nm in a distance of \( d_1 \approx 60 \) nm and the smaller entities of \( r_2 \approx 7.5 \) nm in a distance of \( d_2 \approx 70 \) nm. It should be noted that due to the process of centrifugation during the preparation of CNFs, one filters out larger untreated pulp fibers, so the resulting agglomerates are formed in the film during drying and are not present in the initial dispersion.

In the \( q_z \)-direction, the critical angle is extracted from the decrease above \( \alpha_{crit,CNF} = (0.13 \pm 0.01)^\circ \). The presence of the substrate in our films is negligible, as the intensity observed in Yoneda-region (scattering maximum in the diffuse scattering when the scattering
Figure 4: (a) Intensity distribution along $q_y$ at the Yoneda region of cellulose $\alpha_{\text{crit,CNF}} = 0.13^\circ$ for four different surface charges (black 400 µmol/g, green 800 µmol/g, red 1000 µmol/g, blue 1360 µmol/g). The inset shows the used cylindrical model represented by two different sized cylinders with different distances from each other. For better visualization the graphs are vertically shifted. (b) Intensity distribution as a function of $q_z$ along $q_y = 0 \text{nm}^{-1}$. The dashed magenta line shows the Yoneda region of $\alpha_{\text{crit,H}_2\text{O}} = 0.094^\circ$, the black line shows the critical angle of cellulose.
angle is approximately the critical angle) for silicon $\alpha_{\text{crit, Si}} = 0.137^\circ$ and silica $\alpha_{\text{crit, SiO}_2} = 0.133^\circ$ is low compared to the scattering of the CNF film. Around $\alpha_f = (0.10 \pm 0.01)^\circ$, we observe a narrow intensity increase which can be attributed to a material using the complex X-ray refractive index $n = 1 - \delta + i\beta$. We thus deduce a dispersion of $\delta = 1.49 \times 10^{-6}$ which is in good agreement with water $\delta_{H_2O} = 1.36 \times 10^{-6}$ at a density of $1 \text{ g/cm}^3$ corresponding to a critical angle of $\alpha_{\text{crit, H}_2O} = 0.094^\circ$. Attributing this critical angle to water, it is qualitatively argued that the water content is increasing with surface charge density and is not fully evaporating as assumed due to the high temperature of 100°C applied to the substrate during spray deposition. Sjöstedt et al. could see the same trend in water retention value measurements of TEMPO-CNFS suspensions with increasing surface charge.\textsuperscript{50}

Furthermore, GISANS experiments were performed to elucidate in situ water uptake and release as well as to prove the large scale homogeneity in as prepared CNF thin films. In this context, in situ refers to the fact that the experiments are performed during humidification. AFM measurements confirm that the roughness of $\text{rms} = 4.9 \pm 0.5 \text{ nm}$ is not changed using CNF with 1000 µmol/g for the upscaling to (20 × 100) mm$^2$ wafers. During the GISANS measurements, the CNF thin film with a surface charge of 1000 µmol/g is dried in a humidity controlled measurement chamber to relative humidity (RH) 0%, humidified with $D_2O$ to 90% and redried to 0%. At 90% and 0% RH a GISANS measurement is performed (see Figure 5 (a), Figure S9-S10, Table S5). The 1D intensity distribution is then fitted with the same model used for the PSD similarly to the GISAXS measurements (see Figure 5 (b)). The resulting parameters at the dry state before and after humidification are overlapping within the error bars with the previous measurements, see Table S5. Additionally, due to the larger accessible q-range of the GISANS experiment, a scattering signal from single CNF could be resolved giving one more characteristic scale with a radius of $r_3 \approx 2.5 \text{ nm}$ in a distance of $d_3 \approx 8 \text{ nm}$ which we attribute to the dimensions of the individual CNFs;\textsuperscript{29} for more details see Table S5. Additionally, during humidification we observe that the largest agglomerates of CNFs now appear as spherical objects in the scattering pattern with
Figure 5: (a) Horizontal line cuts of the 2D GISANS data taken at the critical angle for CNF with 1000 µmol/g at \( \alpha_i = 1^\circ \) in a) for the dry, the hydrated (RH 90%), and the redried sample. The pristine and the redried samples are fitted using the cylindrical model approximation on a paracrystal (dashed lines). The intensity difference and the increased intensity at \( \approx 0.2 \text{nm}^{-1} \) in pristine and redried film can be attributed to residual \( \text{D}_2\text{O} \) molecules in the CNF thin film. Due to hydration only the largest entities are changing from a cylinder to a spherical structure, which is schematically illustrated in (b).
no change in radius, but with an increase in distance to each other, see Figure S11 and Table S5. The physical interpretation of the change from a cylindrical to a spherical shape corresponds to the change in structure from two-dimensional to three-dimensional shape. In the present study, only the projection in lateral dimensions is fitted. It should also be noted that the humidification with D$_2$O increased also the contrast within the film. Previous GISAXS measurements by Ehmann et al. who studied the supramolecular rearrangement under HCl influence of trimethylsilyl cellulose, found that either pores inside the film increase in size or increase their distance, as seen in a densification process.\textsuperscript{51} We can confirm that the largest pores or agglomerates increase their separation distance while smaller domains remain constant during humidification. We believe that the large pores or voids are either getting filled during humidification with D$_2$O vapor or D$_2$O condenses at their inner surface; both effects increase increases on the one hand the contrast, as well as a slight expansion on the other hand also let them slightly expand. The smaller features which we observe suggested might seem to be agglomerates of CNF, which do should not vary be changed during humidification. Previous studies have revealed that on the nanoscale, amorphous regions of cellulose\textsuperscript{52,53} are more sensitive to water due to higher accessibility of hydroxyl groups per unit area compared to semi-crystalline CNFs\textsuperscript{54} or crystalline cellulose nanocrystals (CNCs).\textsuperscript{55} However, on the micrometer scale, the accessibility of hydroxyl groups to water also depends on the packing of nanocellulose building blocks, which is highly dependent on processing technique. Langmuir-Schaefer deposition is most favorable in order to induce a high packing density, however at low deposition speed, whereas spin-coating is faster, where the rapid drying kinetics and high shear flows hinder self-assembly of nanocellulose into densely packed structures.\textsuperscript{52} Spray deposition on the other hand, is a highly versatile technique, where packing density and alignment can be tuned by controlling the processing parameters adapting to the requirements for a wide range of applications.\textsuperscript{19,56}
**Wettability**

We expect an influence of the surface charge and roughness on the wetting behavior of the CNF thin film. According to Young’s equation,\(^5^7\) there is a relation between the surface tension of a liquid \(\sigma_{lg}\), the interfacial tension \(\sigma_{sl}\) between a solid (s) and a liquid (l), the contact angle \(\Theta\) and the surface free energy \(\sigma_{sg}\) between a solid and a gas (g),

\[
\sigma_{sg} = \sigma_{sl} + \sigma_{lg} \cdot \cos \Theta
\]  

(1)

According to Owens, Wendt, Rabel and Kaelble,\(^4^2\) one can use the geometrical average of the dispersive (\(\delta\)) and polar (p) components of the surface tensions as:

\[
\sigma_{sl} = \sigma_s + \sigma_l - 2\sqrt{\sigma_s^\delta \sigma_l^\delta} - 2\sqrt{\sigma_s^p \sigma_l^p}
\]  

(2)

Combining Eq. 1 and Eq. 2 yields a linear equation. Using the polar and dispersive components of the used test liquids one can calculate the surface free energy.\(^4^2\) The polar interaction describes the Coulomb interaction between permanent or induced dipoles as hydrogen bonds, while the dispersive interaction stems from van der Waals interactions.\(^5^8\)

We find a nearly constant, slightly decreasing behavior when increasing the surface charge density of the CNF thin film for the dispersive free surface energy (see Figure 6) (red linear fit). Clear changes in the polar component (red circles) of the surface free energy with a maximum at 1000 \(\mu\)mol/g are observed. We conclude that up to a surface charge of 1000 \(\mu\)mol/g the roughness plays the major role in the surface free energy as both the contact angle and roughness decreases simultaneously. At lower roughnesses and increasing surface charge density surface repulsion is dominant in the system (see Figure 3). The total surface free energy is only slightly changed but follows the trend of the polar component. Tailoring the wettability could be crucial for functionalisation of these thin films, e.g. as storage for polar solvents as those are drawing increasing attention in organic photovoltaics as green...
alternative light harvesting material\textsuperscript{59} or in batteries.\textsuperscript{60}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure6.png}
\caption{Free surface energy calculated by the OWRK-method\textsuperscript{42} from the contact angle on the four different cellulose thin films. The data is shown in the individual dispersive (black) and the polar (red) component as well as the total surface free energy (blue). Linear fit of the dispersive component (red line) shows a small minimum at 1000 $\mu$mol/g, marked with the vertical black dashed line.}
\end{figure}

Conventional cellulose fibers as used in paper fulfills all requirements to enable low-cost organic photovoltaics (OPVs), as it is lightweight, biodegradable and inexpensive due to its earth abundant nature. Paper’s biggest advantage is that it is already widely used in large-scale industrial processes e.g. in printing.\textsuperscript{12} We show with spray deposition a fully scalable technique combining all the advantages CNFs nature gives us. Especially for the emerging flexible electronics applications physical properties as low roughness, mechanical strength, porous structure and attraction to liquids are a challenge. Our work shows an approach to further understand and enhance properties as roughness and contact angle. Kontturi et al.\textsuperscript{52} have previously shown that surface roughness of ultrathin amorphous cellulose films had no influence on the contact angle. Elaborating further on the impact of surface charge...
on the contact angle, the Wenzel equation was used to calculate the Young’s contact angle, which is roughness independent (see Figure S12).\textsuperscript{61} An almost linear decrease in the Young’s contact angle is observed that clearly implicating that the contact angle now only dependent on surface charge density. For example, on OPV templates one also need to consider that it needs to provide mechanical strength and does not need to have any intrinsic electronic function. The porous structure of the CNF thin film was elucidated by quantifying the nature of the voids; in addition the change in contact angle as a function of the CNF surface charge, resulting in stratified films of tailored roughness was quantified. The contact angle influences the inhibition behavior of solvents used for depositing or printing functional layers on CNF thin film or nanopapers; the knowledge of both features is thus potentially important for tailoring transparency in OPV applications.

Conclusions

We demonstrate a facile route to prepare large-scale cellulose-based nanostructured thin films with unprecedented low surface roughness down to 2.5 nm on (20 × 100) mm\textsuperscript{2} substrates. We yield a This obtained though the surface topography given by due to a densely packed CNF network. No differences were observed in the layering of the individual CNF while changing the surface charge densities of the fibrils are observed. It can be concluded that increasing ionic strength is highly beneficial for the layering mechanism as it directly influences the self-assembly process, which results in a low roughness. Furthermore, we observed distinct domains of smaller cellulose bundles and larger bundles or agglomerates within the thin film. By studying in situ the humidification and drying of CNFs, we observed that domains reversible change from cylindrical to spherical appearance. With decreasing values of surface roughness corresponding to increasing surface charge densities of CNF films, the surface free energy is observed to be tunable. These features and knowledge can be used to promote the use of polar solvents in applications such as organic solar cells and to further enhance
physical properties and materials lifetime.

Supporting Information

Root-mean-square roughness evaluation; Figure S1, AFM height profile; Figure S2, GISAXS beam damage evaluation; Figure S3, GISAXS translation scan; Figure S4, GISAXS integration region; Figure S5, Contact angle measurements; Figure S6, PSD fitting with cylindrical formfactor approximation; Figure S7, Power spectral density from AFM; Figure S8, GISAXS scattering patterns; Figure S9, GISANS integration region; Figure S10, vertical line cut of the GISANS data; Figure S11, Spherical versus cylindrical approximation fit; Table S1, CNF thickness; Table S2, Polar and dispersive components of test liquids; Table S3, AFM fitting results; Table S4, GISAXS fitting results; Table S5, GISANS fitting results; Table S6, Chemicals.

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Graphical TOC Entry

Reversible structural rearrangements on the nanoscale