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WATER VAPOR UPTAKE OF ULTRATHIN FILMS OF BIOLOGICALLY DERIVED NANOCRYSTALS: QUANTITATIVE ASSESSMENT WITH QUARTZ CRYSTAL MICROBALANCE AND SPECTROSCOPIC ELLIPSOMETRY

The supporting information includes a table showing the relative humidities of the saturated salt solutions and milliQ water used in the QCM-D experiments, raw data from the SE measurements (and modelled film thicknesses) and atomic force microscopy (AFM) height images of the cellulose nanocrystal (CNC) thin films. Also included are explanations of the determination of the dimensions of the CNCs, an example calculation for the water coverage of the hydrated CNC films along with QCM–D data on the water vapor uptake of a pristine silicon dioxide substrate.

EXPERIMENTAL

Table S1. Relative humidities of each saturated salt solution and water used in the QCM–D relative humidity cycles.[1]

Salt	Relative humidity % RH
LiCl	11
$MgCl_2$	33
$Mg(NO_3)_2$	53
NaCl	75
K_2SO_4	97
MilliQ	100

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RESULTS

SE

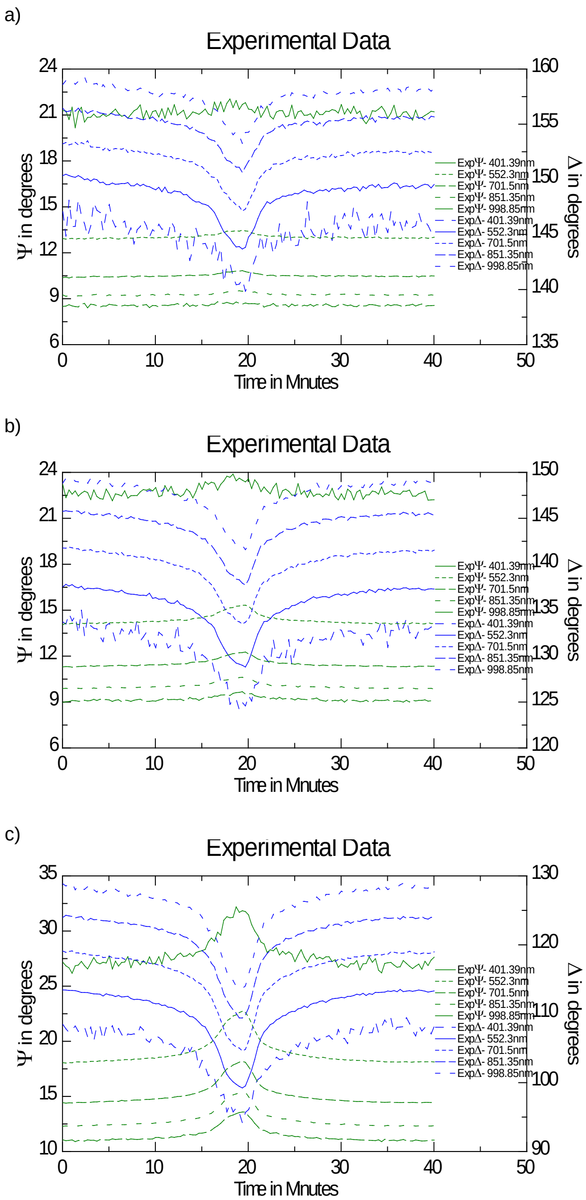

Figure S1. The raw ellipsometric data (Ψ and Δ values) for 5 different wavelengths as a function of the experiment time for a.) 5 gl^{-1}, b.) 10 gl^{-1} and c.) 20 gl^{-1} CNC films. Water adsorption was performed in the 0 – 19 min time range, while desorption was performed in the 19 – 40 minutes time range.

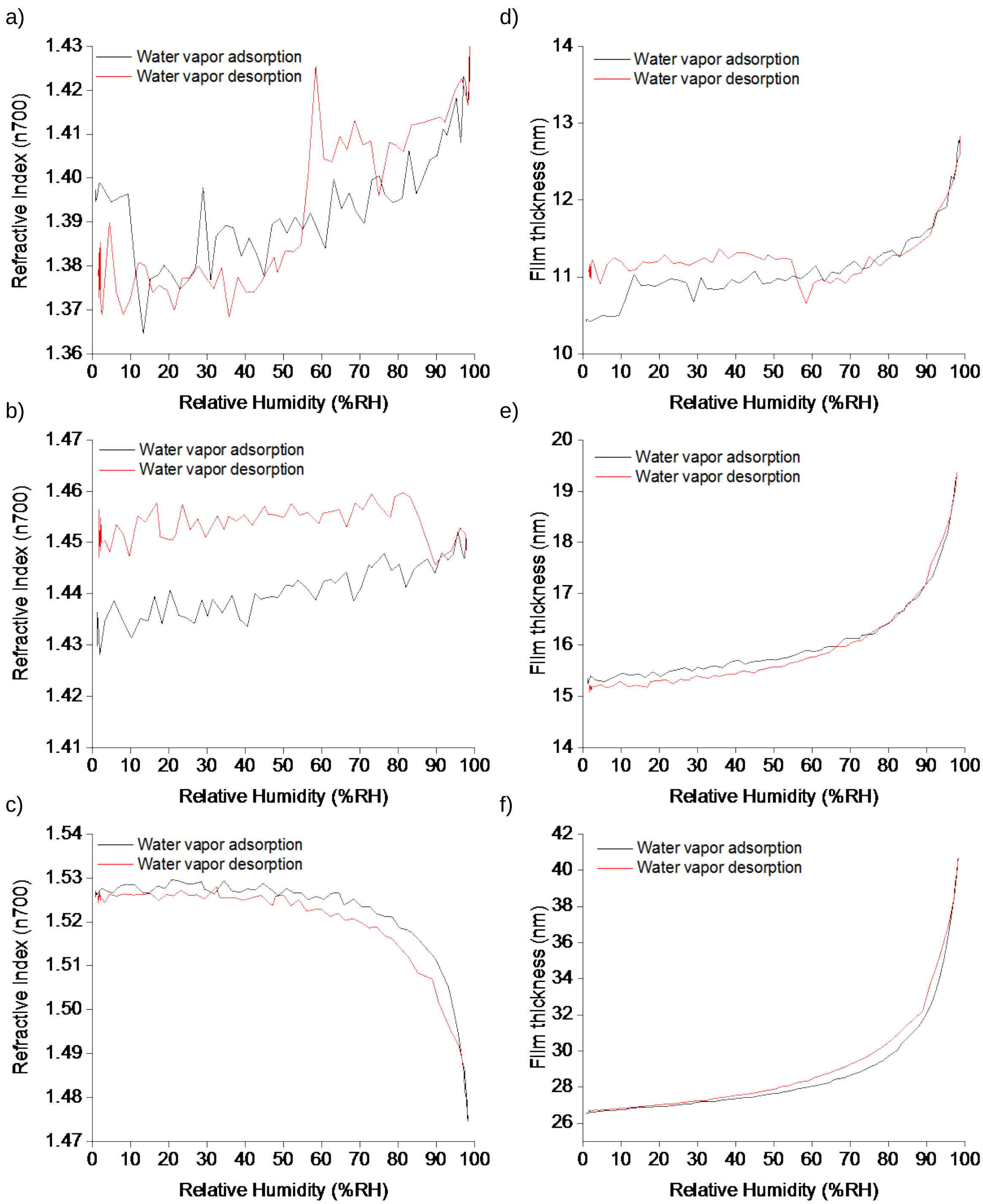

Figure S2. Refractive index as measured by SE (wavelength 700 nm) as a function of %RH for a.) 5 gl^{-1}, b.) 10 gl^{-1} and c.) 20 gl^{-1} CNC films with film thickness modelled using classic Cauchy model from refractive indices for d.) 5 gl^{-1}, e.) 10 gl^{-1} and f.) 20 gl^{-1} CNC films

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AFM

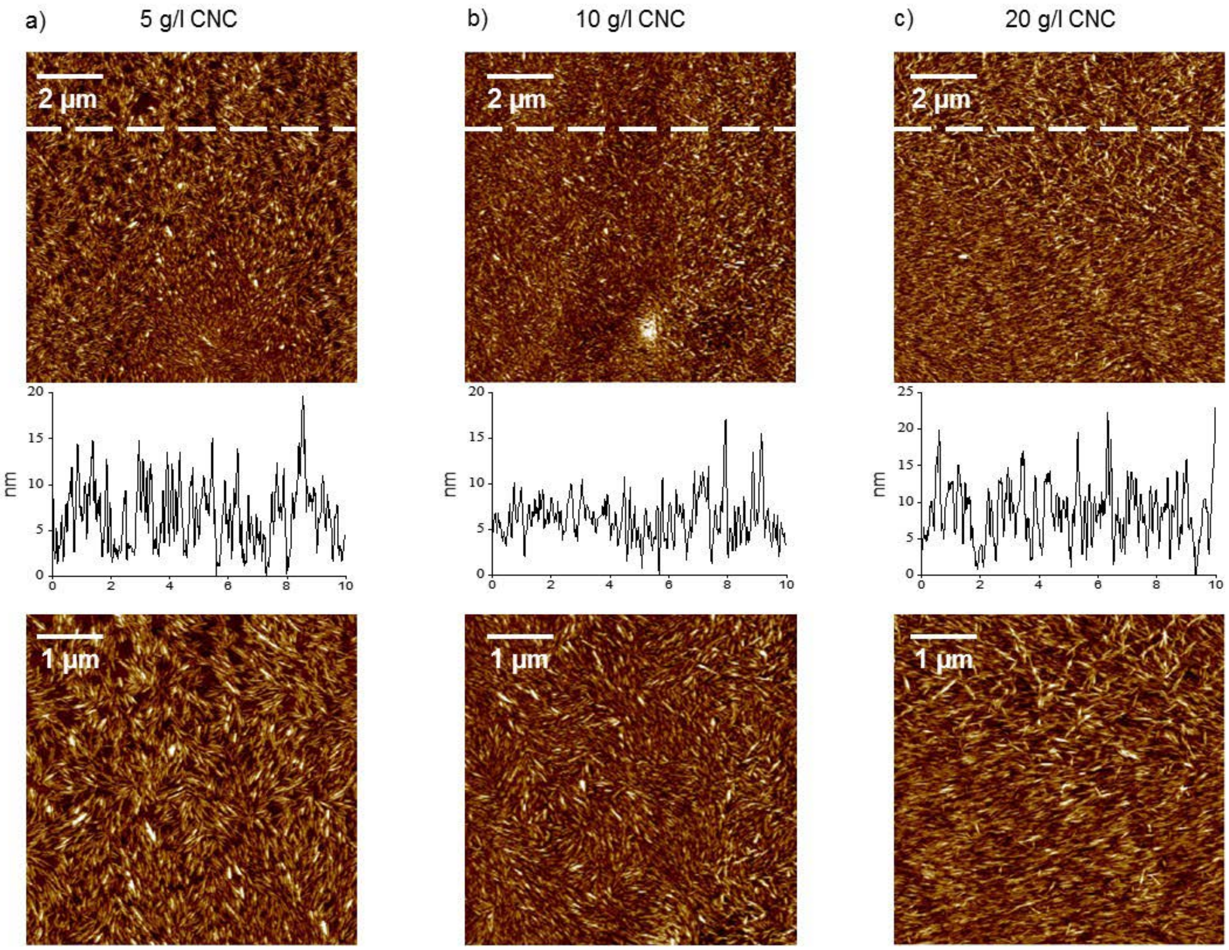

Figure S3. 10 × 10 µm^2 and 5 × 5 µm^2 AFM height images of a) 5 g l^{-1}, b) 10 g l^{-1} and c) 20 g l^{-1} CNC thin films along with height profiles for each 10 × 10 µm^2 image.

SUPPORTING INFORMATION

Table S2. Physical intrinsic properties of CNCs and water used to calculate the water coverage of each CNC in the QCM–D films.

Physical Property	
Bulk density of CNC[2]	1.6 g cm^{-3}
Dimensions of single CNC[a]	7 × 7 × 103 nm^3
Volume of single CNC	5047 nm^3
Surface area of single CNC	2982 nm^2
Thickness of single CNC layer	7 nm
Density of water (23 °C)	1 g cm^{-3}
Surface area of water molecule	0.114 nm^2
Thickness of monolayer of water[3]	0.275 nm

[a] Determined by statistical analysis of AFM image of individual CNCs – see section ‘Determination of CNC Length Distribution’.

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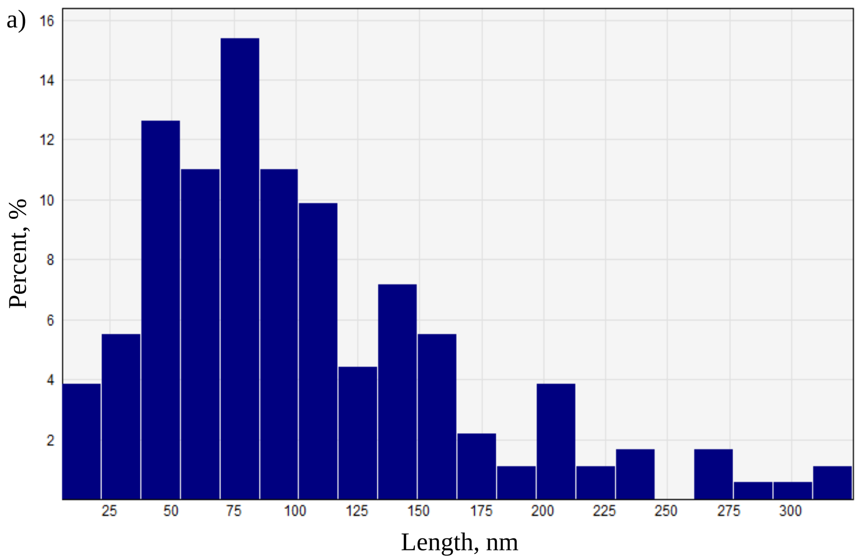
DETERMINATION OF CNC LENGTH DIMENSION

The width of cotton-based CNCs is fairly monodisperse and well reported to be around 7 nm[4]. By contrast, the length of the crystallite varies according to the hydrolysis conditions[5], and therefore, the length distribution of the CNCs used in this study was subjected to scrutiny with AFM. The average length of the CNCs was determined by analyzing an AFM height image of an open CNC film. Analysis was carried out using SPIP 6.0.6 software which, using thresholding, is able to detect each individual CNC in the image and determine its dimensions. The average length for the CNCs was determined to be 103 nm (Figure S4).

a)



b)

Minimum	5.867026 nm
Maximum	324.957653 nm
Mean	102.923595 nm
Std. Dev.	63.087917 nm

c)

Figure S4. a) Length distribution histogram of CNCs determined by image processing, b) statistical data on the length of analyzed CNCs and c) thresholded AFM height image of an open CNC film.

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CALCULATIONS FOR WATER COVERAGE

Underneath is an example of how the coverage of the CNCs in the thin films was calculated based on the QCM–D and SE data attained for the 20 g l^{-1} CNC sample. Physical intrinsic properties of CNCs and water used in calculations can be found in Table S2.

TOTAL SURFACE AREA OF CNCS IN FILM

Surface area of the QCM–D sensor: 0.7854 cm^2 (as provided by manufacturer, Q-Sense)

Initial areal mass of CNC film: 1875.30 ng cm^{-2} = 1.875×10^{-6} g cm^{-2} (From measurement data)

$$\text{Mass of CNC film} = \frac{\text{Initial areal mass of CNC film}}{\text{Surface area of QCM} - \text{D sensory}} = \frac{1.875 \times 10^{-6}\ \text{ng} \cdot \text{cm}^2}{0.7854\ \text{cm}^2}$$
$$= 1.473 \times 10^{-6}\ \text{g}$$

$$\text{Volume of CNC film} = \frac{\text{Mass of CNC film}}{\text{Bulk density of CNCs}} = \frac{1.473 \times 10^{-6}\text{g}}{1.6\ \text{g} \cdot \text{cm}^{-3}} = 9.205 \times 10^{-7}\ \text{cm}^3$$

$$\text{No. of CNCs in film} = \frac{\text{Volume of CNC film}}{\text{Volume of single CNC}} = \frac{9.205 \times 10^{-7}\ \text{cm}^3}{(7 \times 7 \times 103)\ \text{cm}^3} = 1.824 \times 10^{11}\ \text{CNCs}$$

$$\text{Total surface area of CNCs in film} = \text{No. CNCs in film} \cdot \text{surface area of single CNC}$$
$$= 1.824 \times 10^{11} \cdot 2982\ \text{nm}^2 = 5.439\ \text{cm}^2$$

TOTAL SURFACE AREA OF WATER IN FILM

Areal mass of swollen CNC system (97 %RH): 2407.59 ng cm^{-2} = 1.875×10^{-6} g cm^{-2} (From measurement data)

Areal mass of water in CNC system = 532.29 ng cm^{-2} = 5.32×10^{-7} g cm^{-2} (difference between initial areal mass of CNC film and swollen CNC film (97 %RH))

Areal mass of water adsorbed by pristine substrate (silicon dioxide sensor) (97 %RH) = 8.68×10^{-8} g cm^{-2} (Figure S5c).

SUPPORTING INFORMATION

Areal mass of water in CNC film = 4.45×10^{-7} g cm^{-2} (difference between areal mass of water in CNC network and water adsorbed by pristine substrate (97 %RH))

$$\text{Mass of water in CNC film} = \frac{\text{Areal mass of water in CNC film}}{\text{Surface area of QCM} - \text{D sensory}} = \frac{4.45 \times 10^{-7}\ \text{g} \cdot \text{cm}^2}{0.7854\ \text{cm}^2}$$

$$= 3.50 \times 10^{-7}\text{g}$$

$$\text{No. of moles of water in CNC film} = \frac{\text{Mass of water in CNC film}}{\text{RMM}_{\text{H}_2\text{O}}} = \frac{3.50 \times 10^{-7}\text{g}}{18}$$

$$= 1.94 \times 10^{-8}\ \text{mol}$$

$$\text{No. of water moleules CNCs in film} = \text{no. of moles of water} \cdot \text{N}_\text{A}$$

$$= 2.32 \times 10^{-8}\ \text{mol} \cdot 6.022 \times 10^{23}\ \text{mol}^{-1} = 1.17 \times 10^{16}\ \text{molecules}$$

$$\text{Total surface area of water in CNC film}$$

$$= \text{No. water molecules in CNCfilm} \times \text{surface area of single water molecule}$$

$$= 1.17 \times 10^{16} \cdot 0.114\ \text{nm}^2 = 13.34\ \text{cm}^2$$

WATER COVERAGE OF EACH CNC IN FILM

$$\text{Water coverage of each CNC in film} = \frac{\text{Total surface area of water in CNC film}}{\text{Total surface area of CNCs in film}} = \frac{13.34\ \text{cm}^2}{5.439\ \text{cm}^2}$$

$$= 2.45\ \text{monolayers}$$

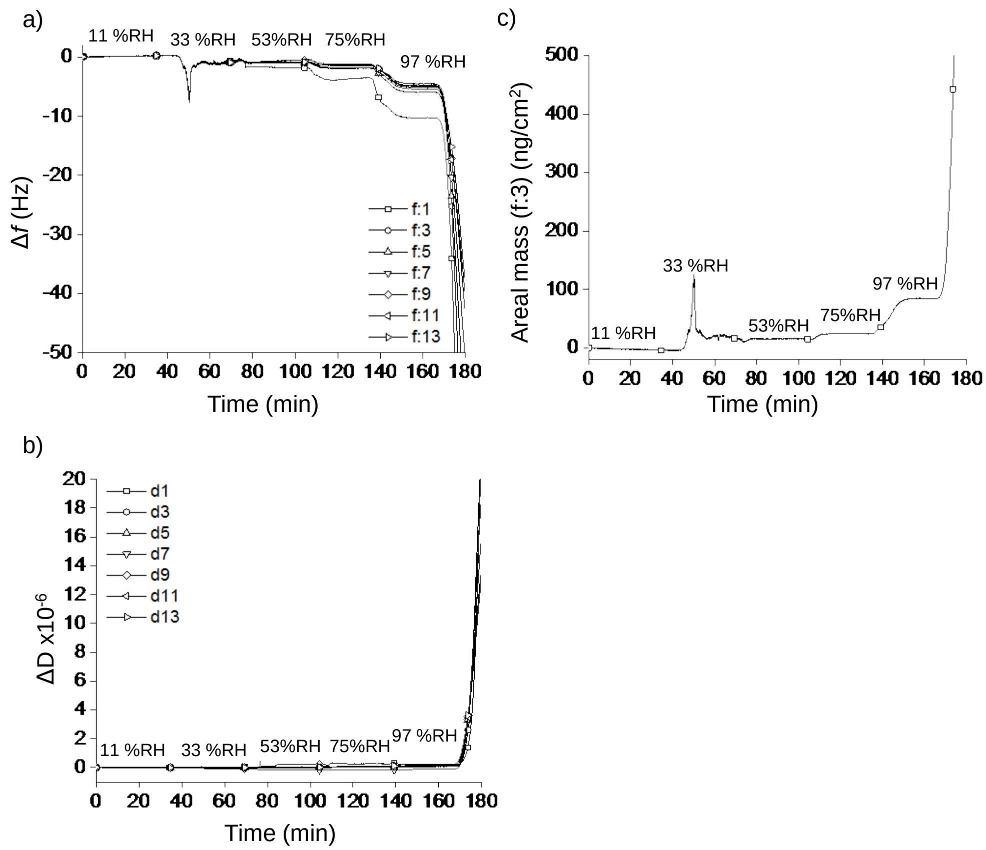

Figure S5. Water vapor uptake behavior of pristine silicon dioxide QCM-D crystal, a.) Δ*f*, b.) ΔD and c.) areal mass of crystal with increasing %RH.

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REFERENCES

(1) Greenspan, L. Humidity Fixed Points of Binary Saturated Aqueous Solutions. *J. Res. Natl. Bureau Stand.* **1977**, *81*, 89–96.

(2) Heath, L; Thielemans, W. Cellulose nanowhisker aerogels. *Green Chem.*, **2010**, *12*, 1448–1453.

(3) Pierotti, R.A. Aqueous solutions of nonpolar gases. *J. Phys. Chem.*, **1965**, *69*, 281–288.

(4) Majoinen, J.; Walther, A.; McKee, J.R.; Kontturi, E.; Aseyev, V.; Malho, J.M.; Ruokolainen, J.; Ikkala, O. Polyelectrolyte brushes grafted from cellulose nanocrystals using Cu–mediated surface–initiated controlled radical polymerization. *Biomacromolecules*, **2011**, *12*, 2997–3006.

(5) Dong, X.M.; Revol, J.–F.; Gray, D.G. Effect of microcrystalline preparation conditions on the formation of colloid crystals of cellulose. *Cellulose*, **1998**, *5*, 19–32.