Aggregation Behavior of Aqueous CNC Cellulose Nanocrystals. The Effect of Inorganic Salts

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SUPPORTING INFORMATION

1. Determination of the CNC length and thickness by DLS and DDLS:

The dynamics properties of the CNC rod-like particles in a dilute suspension are investigated using polarized and depolarized dynamic light scattering (DLS and DDLS). The polarized and depolarized time correlation function for monodisperse cylinder in a dilute suspension are related to the rotational and translational diffusion coefficients of the particle by:

$$I_{vv}(q,t) = \langle N \rangle \alpha_{iso}^2 \exp\left(-q^2 D t\right) + \frac{4}{45} \langle N \rangle \alpha_{aniso}^2 \exp\left[-\left(q^2 D + 6\Theta\right)t\right] \quad \text{(S1)}$$

$$I_{vh}(q,t) = \frac{1}{15} \langle N \rangle \alpha_{aniso}^2 \exp\left[-\left(q^2 D + 6\Theta\right)t\right] \quad \text{(S2)}$$

where $\langle N \rangle$ is the average number of particles in the scattering volume, α_{iso} is the isotropic part of the polarizability tensor, and α_{aniso} is the molecular optical anisotropy.

Figure S1 shows the polarized DLS (a) and depolarized DLS (b) at several scattering angles for CNC suspension at very dilute concentration C = 0.01 g/l. The solid lines are the best fits to the Eq.5. In the figure S2, the relaxation frequencies are obtained from the fitting procedure and are plotted as a function of the square of scattering wave vector q^2. The solid line in figure S2a is a linear fit through origin. Translational diffusion coefficient can be

obtained from the slope of the line. In figure S2b, rotational diffusion coefficient can be deduced from the intercept of the solid line.

The translational and rotational diffusion coefficients of a rigid rod are related to the length and the cross section diameter by the Broersma relation. The translational diffusion coefficient is:

$$D = \left(\frac{k_b T}{3\pi\eta L}\right)\left[\delta - \frac{1}{2}\left(\gamma_{\parallel} - \gamma_{\perp}\right)\right] \qquad \text{(S3)}$$

with $\delta = \ln\left(2\frac{L}{d}\right)$,

$$\gamma_{\parallel} = 0.807 + \frac{0.15}{\delta} + \frac{13.5}{\delta^2} - \frac{37}{\delta^3} + \frac{22}{\delta^4} \text{ , } \gamma_{\perp} = -0.193 + \frac{0.15}{\delta} + \frac{8.1}{\delta^2} - \frac{18}{\delta^3} + \frac{9}{\delta^4}$$

The rotational diffusion coefficient is given by

$$\Theta = \left(\frac{3k_b T}{\pi\eta L^3}(\delta - \xi)\right) \qquad \text{(S4)}$$

with $\xi = 1.14 + \frac{0.2}{\delta} + \frac{16}{\delta^2} - \frac{63}{\delta^3} + \frac{62}{\delta^4}$

The length L and the diameter d of the CNC particle are found L = 170 nm and d = 17 nm using eqs S3 and S4.

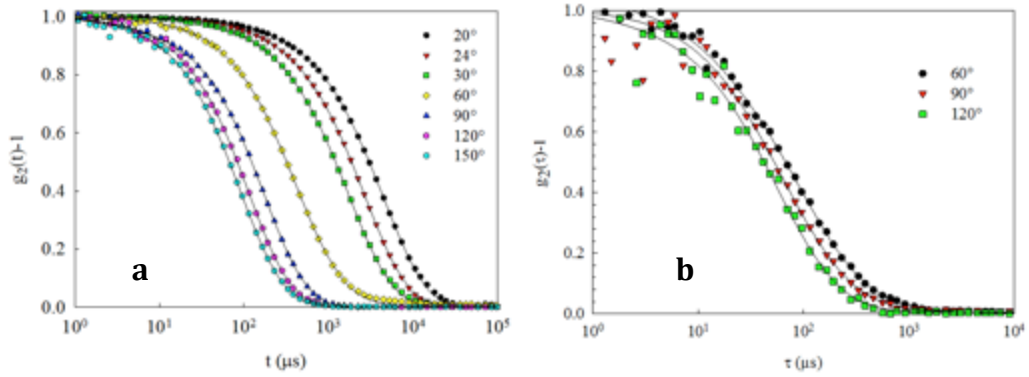

Figure S1. Autocorrelation functions measured at the different angles for CNC suspensions at a concentration of 0.01 g/l in $\boldsymbol{I}_{VV}$ (a) and I_{VH} (b) detection.

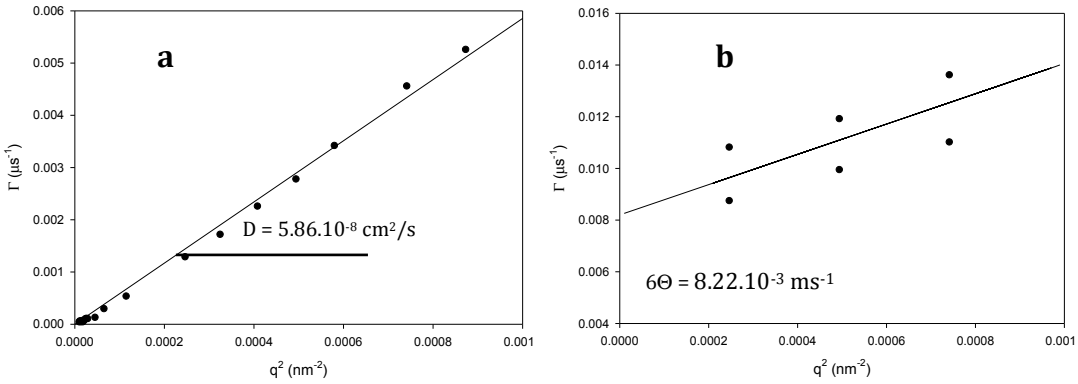

Figure S2. Variation of the extracted relaxation frequencies from polarized DLS (a) and depolarized DDLS (b) at different scattering angles as a function of q^2 for the NCC suspension at a concentration of 0.01 g/l. The solid line in figure S2a is a linear fit through origin. Translational diffusion coefficient can be

obtained from the slope of the line. In figure S2b, rotational diffusion coefficient can be deduced from the intercept of the solid line.

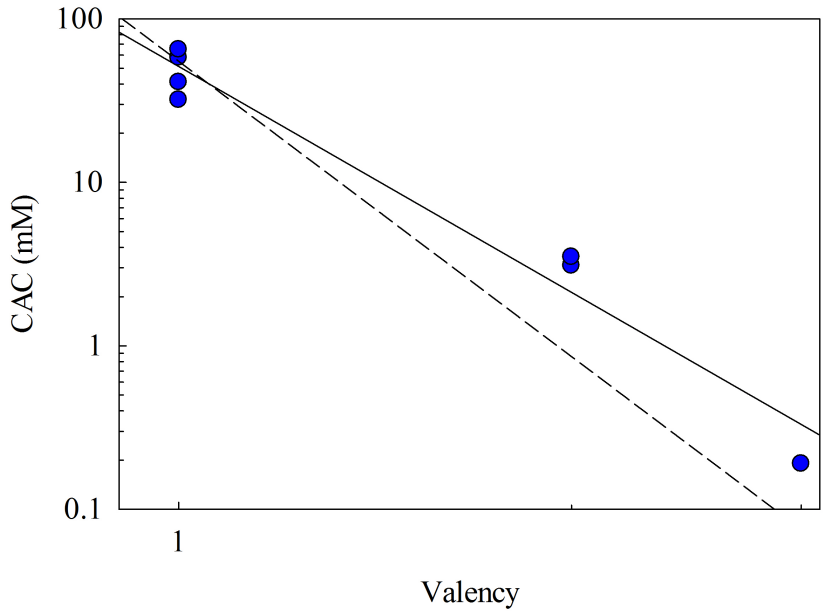

Figure S3. Evolution of the critical aggregation concentration of 0.67 g/l CNC suspension as a function of cation valence. The solid line is a linear fit through experimental data. The dash line is a Schulze-Hardy prediction.

2. Static light scattering

Static light scattering (SLS) measurements were performed on a ALV/CGS-8F (Germany). The light source was a solid-state laser, with a wavelength λ = 532 nm, and the sample temperature was controlled by a thermostat bath to 20 ± 0.2 °C. Toluene has been used as an index matching liquid. Measurements were made at angles of observation (θ) between 12 and 150 degrees. The relative scattering intensity (I_r) was calculated as the difference between the sample intensity and the solvent scattering divided by the scattering intensity of toluene at 20°C. I_r is related to the weight average molar mass (M_w) and the scattering wave vector (q) dependent structure factor ($S(q)$) of the solute (Brown 1996; Nicolai 2007):

$$\frac{I_r}{KC} = M_w S(q) \qquad \text{(Eq. S5)}$$

with C being the particle concentration (g.mL^{-1}) and K being an optical constant depending on the refractive index increment, where we used an increment of 0.103 mL.g^{-1} considering that the refractive index of cellulose is 1.5

The CNC particles were diluted in 10mM NaCl to minimize the electrostatic interaction between rods. In dilute solutions, $S(q) = P(q)$ where $P(q)$ is the form factor of the solute. For a rod with the radius R and the length L oriented in the direction of angle α with respect to the referential axis, the form factor is given by:

$$P_{rod}(q,\alpha) = \left[\frac{2J_1(qR\sin\alpha)}{qR\sin\alpha}\frac{\sin q(L/2)\cos\alpha}{q(L/2)\cos\alpha}\right] \qquad \text{(Eq. S6)}$$

where $J_1(x)$ is a first order Bessel function. If the rods are randomly oriented in the space, the form factor should be taken as an average in all directions, and then Eq. 3 becomes:

$$P_{rod}^{random}(q,\alpha) = \int_0^{\pi/2} \sin\alpha \, d\alpha \; P_{rod}(q,\alpha) / \int_0^{\pi/2} \sin\alpha \, d\alpha \qquad \text{(Eq. S7)}$$

Figure S4 shows the evolution of normalized intensity as a function of the wave vector q for the CNC suspension at a dilute particle concentration, 0.01g/l. An average molar mass of $M_w = 5 \cdot 10^7$ g.mol^{-1} was determined from the fit of the data. The evolution of the structure factor, S(q), at high q did not follow a q^{-1} dependence as expected in the case of rod like particles. An obvious reason for this deviation is the contribution from polydispersity, which results from the preparation route that is mostly a diffusion-controlled acid hydrolysis.

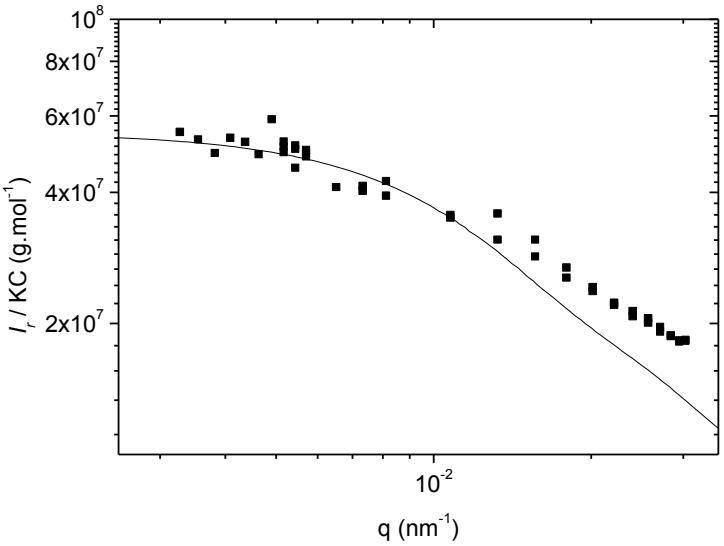

Figure S4. Normalized intensity Ir/KC as a function of wave vector q for the CNC suspension at C = 0.01 g/l. The solid line is the fit with a rod-like particle form factor (Eq. S7).

3. Characterization of CNC by AFM

A Ntegra, NT-MDT atomic force microscope, with Nova software, was used. The surface was scanned in semi-contact mode with a speed of 1.01 Hz using a cantilever, NSG01, from NT-MDT. Images were further processed with the software Gwyddion.
The samples of CNC were prepared as follows. A 1x1 cm^2 mica plate was covered with a 20 µL drop of 0.1 wt% polyethyleneimine, PEI, for 3 minutes and subsequently rinsed with water and dried with nitrogen gas. A 20 µL drop of the sample, 0.05 wt%, was placed on the surface and the same drying procedure as for the PEI was applied.

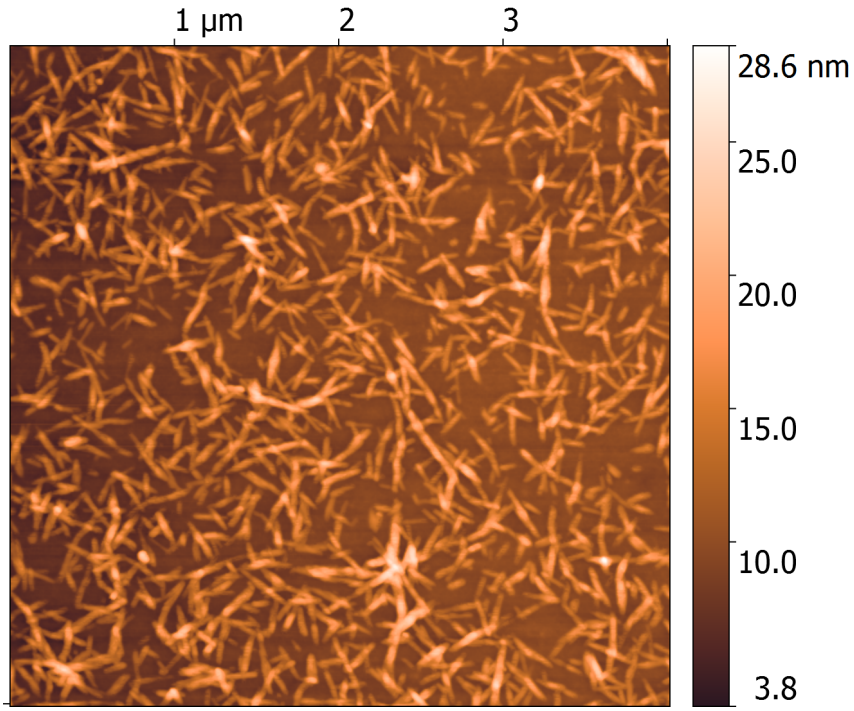

Figure S5. AFM micrograph of CNC deposited (0.05 wt%) on mica pre-coated with 0.1 wt% aqueous solution of PEI (40 000 g/mol).

References

Brown W (1996) Light Scattering: Principles and Development Monographs on the Physics and Chemistry of Materials. Clarendon Press, Oxford

Nicolai T (2007) Food structure characterisation using scattering methods. In: McClements DJ (ed) Understanding and controlling the microstructure of complex foods. Woodhead: Cambridge, pp 288– 310