Supplementary Information (SI) for Nanoscale Advances.

Supporting Information

Tuning the phase separation of cellulose nanocrystals with hydrolysis times: Influence of effective dimensions

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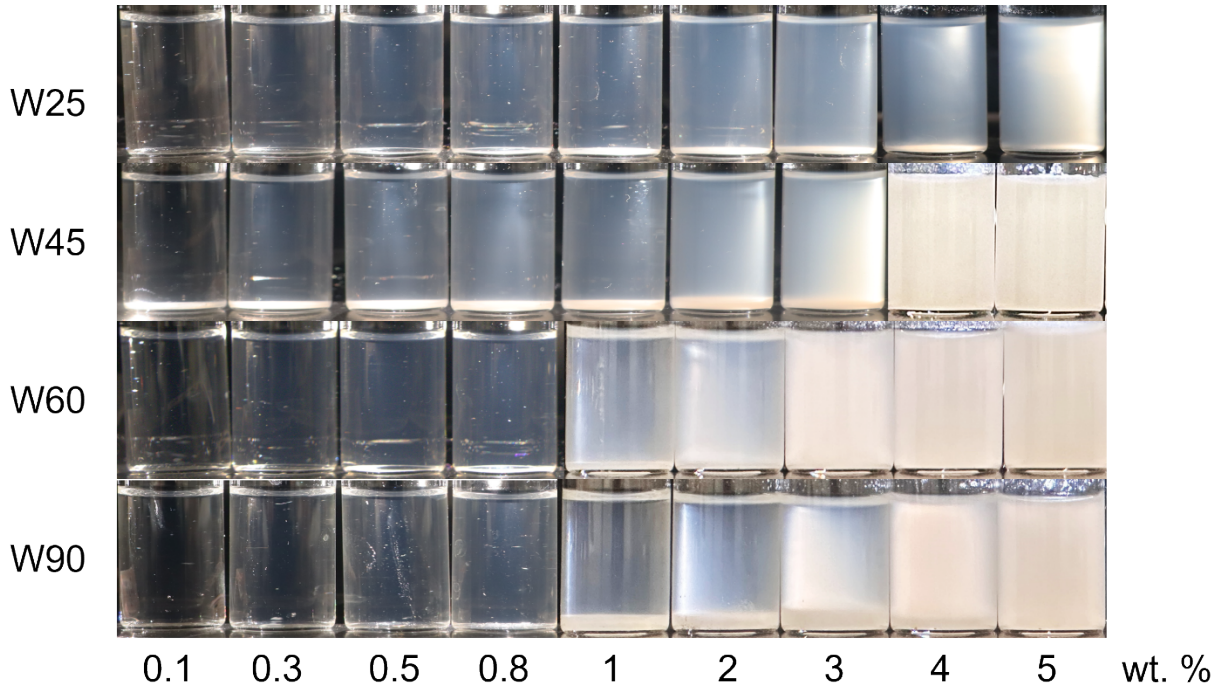

Figure S1. Replicated phase separation of CNC suspensions prepared from different hydrolysis times (25, 45, 60, and 90 min) at different weight concentrations.

Tabel S1. Error analysis for surface charge of CNC suspensions prepared at different hydrolysis times (25, 45, 60, and 90 min).

Sample	Mean	Std Dev	Std Error	95% Confidence interval (CI) (±)	95% CI (Lower – Upper)
W25	107.19	2.32	1.34	5.76	101.43 – 112.95
W45	142.39	8.44	4.87	20.97	121.42 – 163.36
W60	139.62	7.5	4.33	18.63	120.99 – 158.25
W90	164.28	11.17	6.45	27.75	136.53 – 192.03

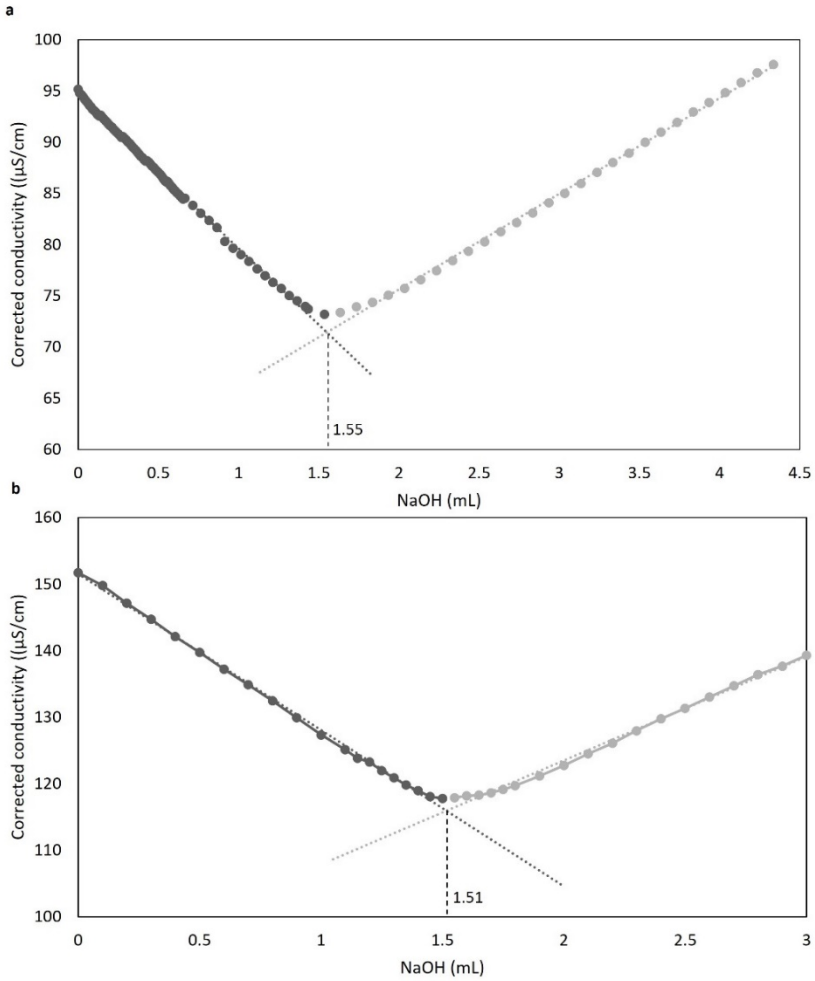

Figure S2. Examples of conductometric titration curves (standard CSA Z5100-14) of the cellulose nanocrystal suspension W25 (prepared at a hydrolysis time of 25 min) without (a) and with (b) strong acid cation exchange resin (SAC) treatment.

Area-equivalent (AE) diameter and rectangularity (R)

The AE diameter and rectangularity, R, were calculated using the method described by Parton et al.[1]. The cellulose nanocrystal (CNC) particles with irregular shapes are fitted into a bounding rectangle with boundary length (l_t) and diameter (d_t), as illustrated by the red boxes in Fig. S3

However, these boundary dimensions do not adequately capture the actual morphology of the CNC particles. The AE diameter is determined by dividing the projected area on TEM images by the boundary length: $d_{AE} = A/l_t$ as illustrated in Fig. S3 (green square). The rectangularity is given by: $R = d_{AE}/d_t$.

According to Parton et al.[1], CNC particles can be categorized into four types based on the AE diameter and rectangularity: aggregates (high d_{AE} and low R), bundles (high d_{AE} and high R), crystallites (low d_{AE} and high R), distorted crystallites (low d_{AE} and low R). The boundary of d_{AE} is defined as twice the average diameter of a single crystallite, which is 23 nm in this study. The boundary of R is set at 0.5, determined from the R distribution in Fig. 3a.

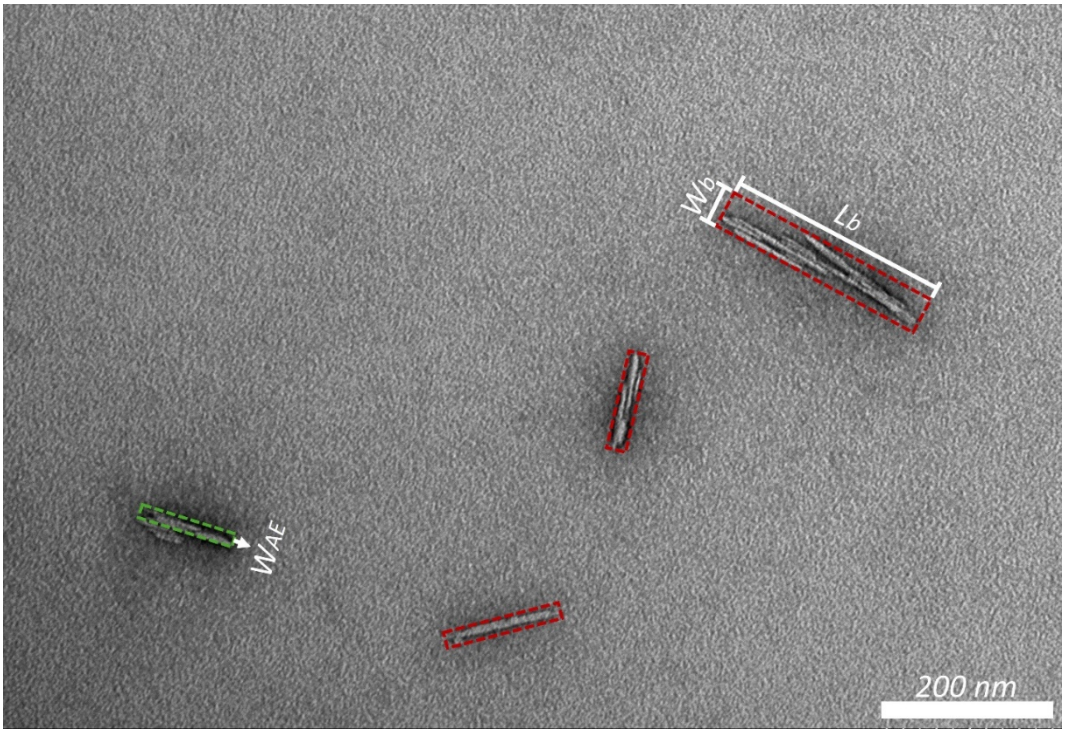

Fig S3. Transmission electron microscope (TEM) images of CNC particles prepared for 45 minutes by sulphuric acid hydrolysis. The red boxes illustrate the measurement of boundary length and boundary diameter. The green box illustrates the AE diameter.

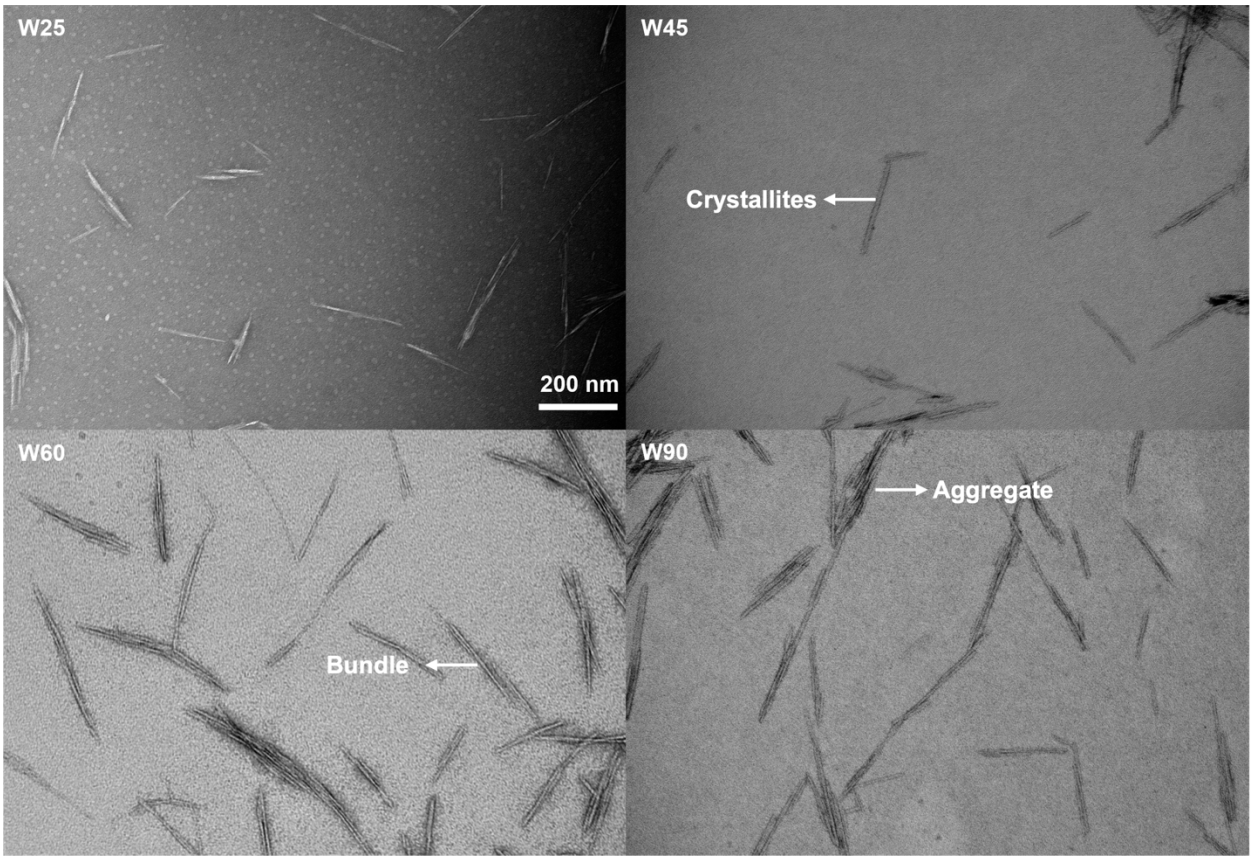

Figure S4. Transmission electron microscopic (TEM) images of CNC suspensions prepared from different hydrolysis times (25, 45, 60, and 90 min).

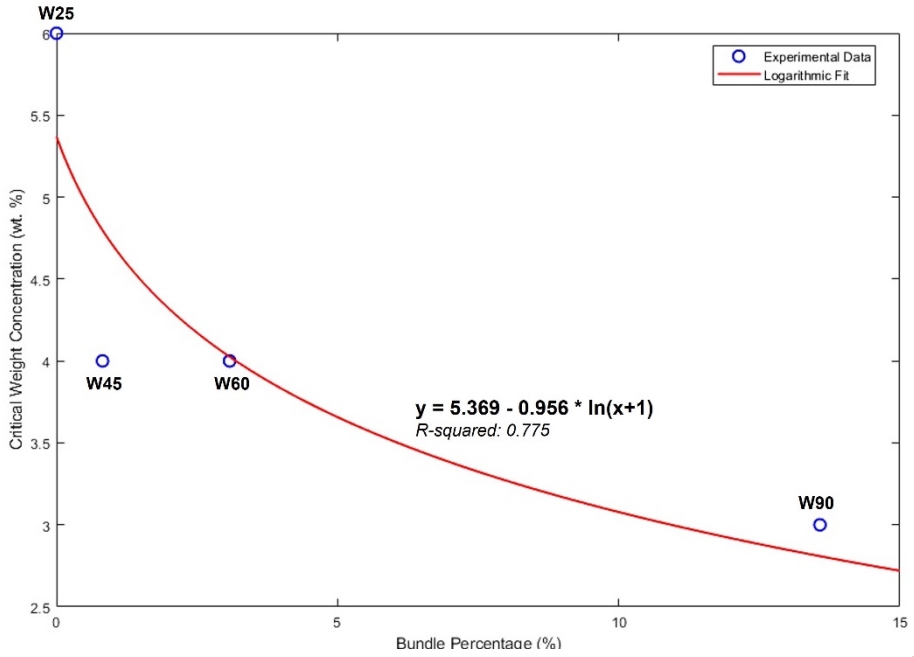

Figure S5. Relationship between critical weight concentration and bundle percentage fitted with logarithmic regression.

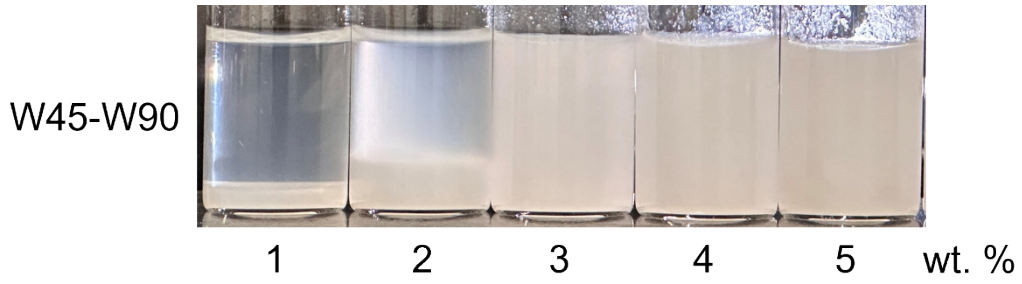

Figure S6. Phase separation of mixed W45 and W90 CNC suspensions at different weight concentrations (1 – 5 wt.%). The mixing ratio of W45 and W90 is 1:1.

Theoretical critical weight concentration

The Debye length is calculated as follows (Eq. 1):[2]

$$\kappa^{-1} = \frac{0.304}{\sqrt{I(M) + I_{ci}(M)}} \#(1)$$

where I is the ionic strength of the solution, which accounts for both the free electrolytes in the solution $I(M)$ and the counterions associated with the charged colloidal particles $I_{ci}(M)$.[3]

Since no additional electrolytes were introduced into the CNC suspensions, the H^+ counterions only are considered.

The amount of counterions is inferred from the charged groups present on the CNC surface. The ionic strength from the counterions (I_{ci}) is determined by (Eq. 2):

$$I_{ci} = \frac{\Gamma z_{ci}^2 c_{ci} x 10^{24}}{N_A} \#(2)$$

where z_{ci} is the valence of counterion, c_{ci} is the concentration of counterions (nm^{-3}), and N_A is Avogadro's number $6.02x10^{23}$ (mol^{-1}).

The Donnan salt exclusion coefficient (Γ) is given by (Eq. 3):[3]

$$\lim_{I \to 0} \Gamma = \begin{cases} \frac{1}{2}\left(1 - \frac{1}{2}\xi\right), \xi < 1 \\ \frac{1}{4\xi}, \xi > 1 \end{cases} \#(3)$$

where $\xi = \frac{Q}{l_{eff}} = \frac{Q v_{eff}}{e}$.

Here, l_{eff}, the effective distance between two elementary charges $\pm e$ along the particle long axis, is approximately 0.26 nm in this study. Q is the Bjerrum length (0.714 nm in water at 25° C), and v_{eff} is the effective linear charge density. For this case, $\xi > 1$.

The concentration of counterion (c_{ci}) is given by[4]

$$c_{ci} = \gamma c_p \#(6)$$

where γ is the number of charged sites on each CNC rod, c_p is the number density concentration of CNC rods in the suspension, calculated as follows (Eq. 7):

$$c_p = \frac{w}{\left(w + (100 - w)\frac{\rho_{CNC}}{\rho_{sus}}\right)V} \#(7)$$

where w is the weight concentration of CNCs, $\rho_{CNC}$is the density of cellulose (1.6 g/cm^3), ρ_{sus} is the density of the suspension (1 g/cm^3), and V is the volume of each CNC (assumed as a cylinder).

The effective diameter can be expressed as (Eq. 8):[3,4]

$$d_e = d + \kappa^{-1}\left(lnA^{'} + 0.7704\right) \#(8)$$

where d is the actual diameter of CNCs (average diameter measured from TEM), $A^{'}$ is given by (Eqs. 9 and 10):

$$A^{'} = 2\pi v_{eff}^2 Q \kappa^{-1} e^{-\kappa d} \#(9)$$

$$v_{eff} = \frac{2\pi\sigma}{\kappa K_1\left(\frac{\kappa d}{2}\right)} \#(10)$$

where σ is the surface charge density (e/nm^2), and K_1 is the first order Bessel function.

According to Onsager's theory, the anisotropic phase begins to develop when[5]

$$bc_{ci} = b\frac{N_{ItoN}}{V_{sus}} = 3.3 \#(11)$$

where N_{ItoN} is number of particles at the onset of nematic phase, and b is the co-volume of the particles in a solution (the space excluded by the particles in a solution), given by (Eq. 12):

$$b = \frac{\pi}{4} l^2 d_e \#(12)$$

with l, the average length of CNCs measured from TEM images.

Therefore, the critical effective volume fraction, $\phi_{0'}$ at the onset of anisotropic phase is calculated as (Eq. 13):

$$\phi_0 = \frac{N_{ItoN} V_e}{V_{sus}} = 3.3 \frac{\frac{\pi}{4} d_e^2 l}{\frac{\pi}{4} l^2 d_e} = 3.3 \frac{d_e}{l} \#(13)$$

Finally, the critical weight concentration, $w_{0,}$ is given by (Eq. 15):

$$w_0 = 3.3 \frac{\rho_{CNC}\, d^2}{\rho_{sus}\, d_e l} \#(14)$$

Given the surface charge density and the dimension of CNCs, d_e can be determined as a function of the weight concentration using Eqs. 1-10. The critical weight concentration, w_0, can then be calculated by solving Eq. 14.

Table S2. Calculated Debye length and effective diameter, d_e, of CNCs.

CNC suspensions	Hydrolysis time (min)	Average length (nm) [std]	Average AE diameter (nm) [std]	Debye length (nm)	Effective diameter (nm)	Calculated w_0 (%)
W25	25	239.90 [110.48]	8.35 [3.94]	49.89	495.28	0.65
W45	45	148.85 [73.39]	8.59 [4.21]	25.41	245.67	1.24
W60	60	271.91 [148.25]	12.70 [5.71]	27.19	304.18	1.20
W90	90	244.93 [116.04]	16.28 [8.76]	13.81	165.45	3.76

References

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