

Supplementary Information for

Nanostructural Properties and Twist Periodicity of Cellulose Nanofibrils with Variable Charge Density

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Supplementary text

Fibril characterization using AFM

To make sure that we were able to compare the AFM images with as little bias as possible, we only tracked single fibrils without splitting events or thick segments where two or more fibrils overlay. The concentration for the different fibril dispersions used to adsorb the fibrils onto mica was adjusted to guarantee the least possible overlapping. The adsorption on the mica depends on the charge density as well as the sonication time and could be seen as a qualitative measurement for the effectiveness of the fibrillization. Depending on the sonication time, the number of larger particles (agglomerates and fibrils that split) not taken into account were around 50% for 5 min of sonication. This value declined to around 25% for 17 min of sonication. However, the variation between the data of a completely tracked image (100% of the fibrils) and the data we presented in the paper is lower than 3%.

Crystallinity due to WAXS

As an average of all measured samples, we got around 69% crystallinity before sonication (including pulp with and without TEMPO-mediated oxidation) and 58% crystallinity after the sonication treatment for bleached pulps (Table S2). For the unbleached samples, we did less measurements and a difference before and after sonication is less distinctive, 68% before and 64% after sonication.

Supplementary figures

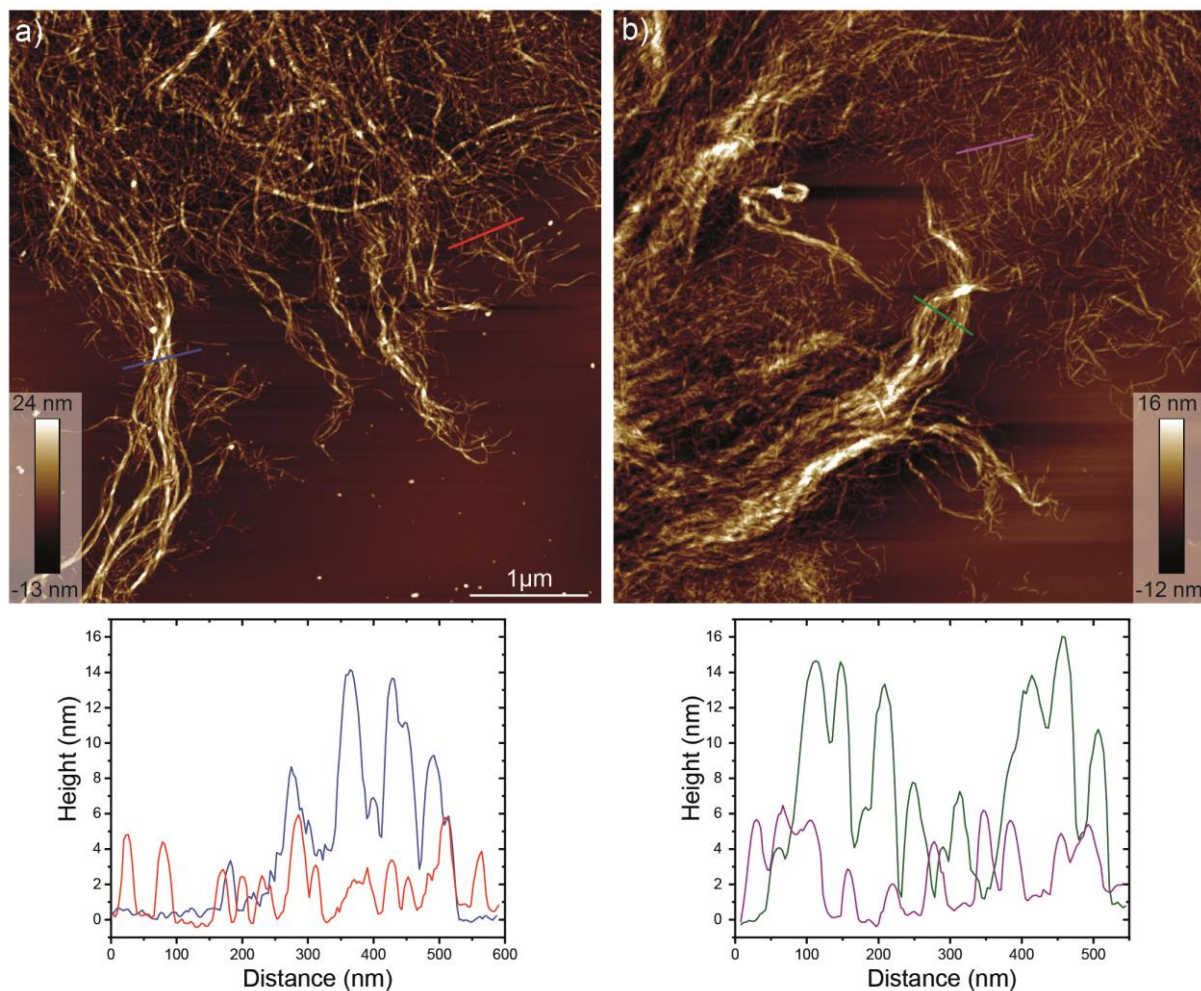


Figure S1. AFM images of TEMPO-mediated oxidized a) unbleached and b) bleached paper pulp without sonication treatment and the corresponding height profiles along the colored lines at the bottom of each image.

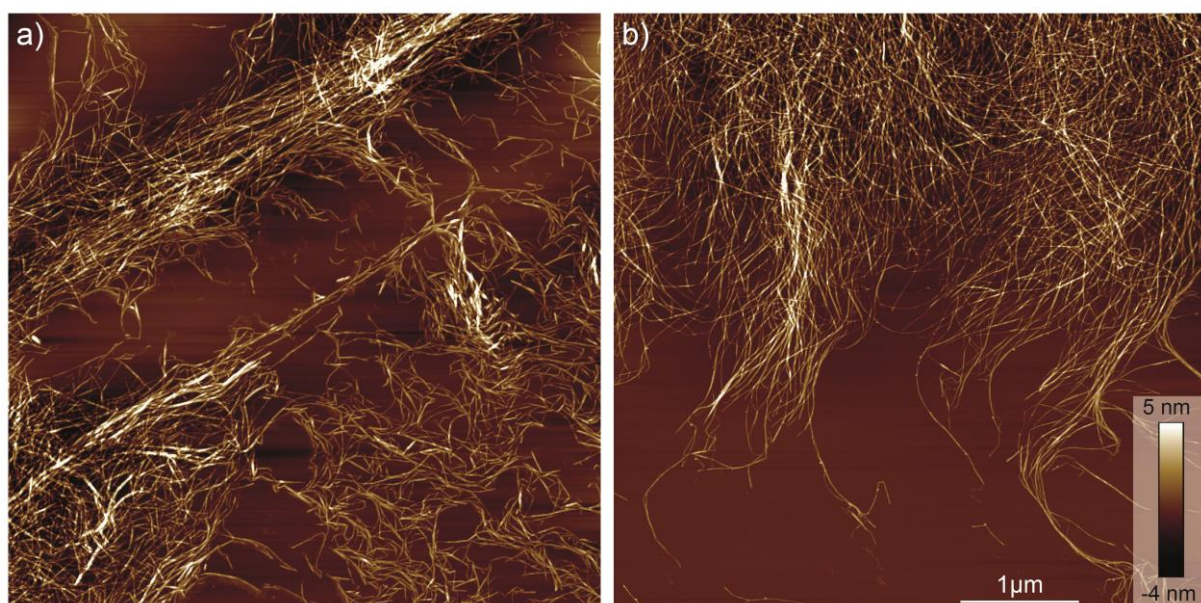


Figure S2. AFM images of the pellet from the centrifugation after sonication treatment of a) unbleached and b) bleached TEMPO-mediated oxidized pulp.

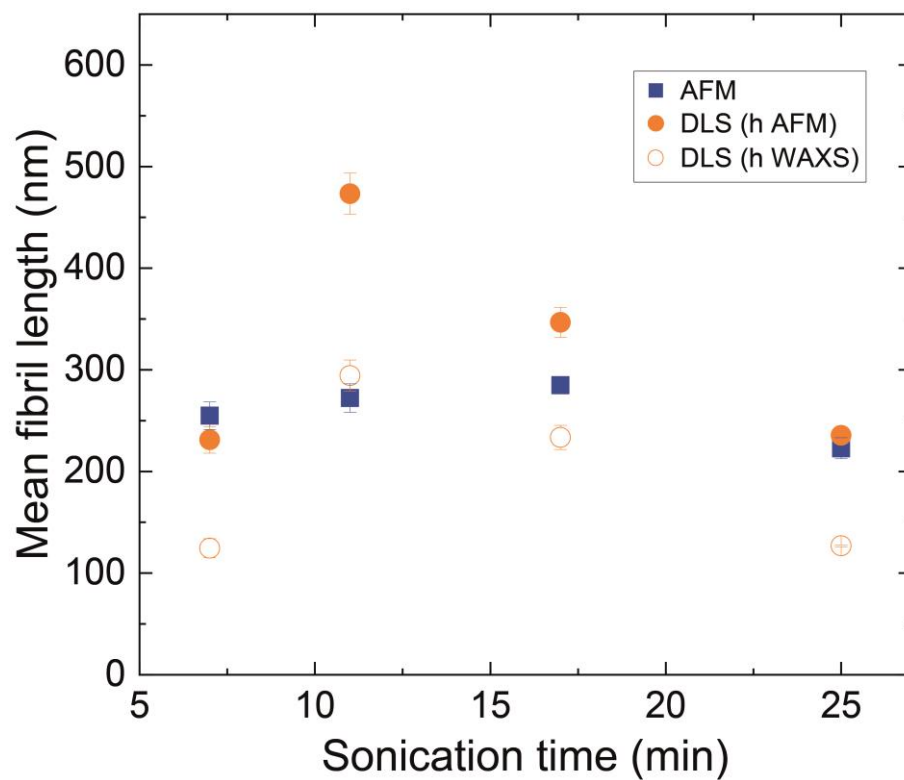


Figure S3. Comparison of mean fibril length between DLS (orange circle) and AFM (blue square) measurements of CNF dispersions prepared from bleached wood pulp with a charge density of 830 $\mu\text{mol/g}$ CNF (standard deviation of DLS of 3 measurements and standard error of AFM $n > 200$). For DLS the height h is taken from either AFM ($h \approx 2$ nm, full circle) and WAXS ($h \approx 4$ nm, empty circle), respectively.

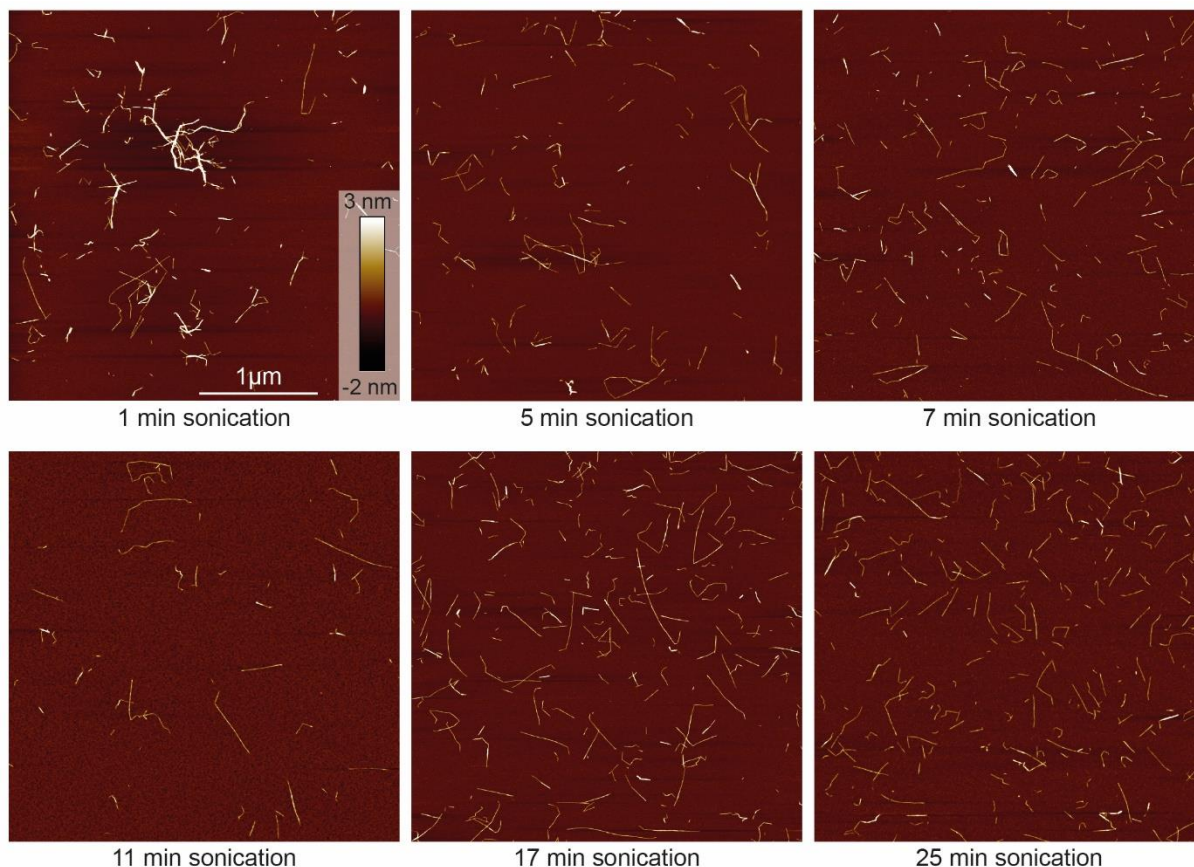


Figure S4. Representative AFM images showing the influence of increasing sonication time on the fibrillation of CNFs from bleached paper pulp with a charge density of $830 \mu\text{mol/g}$.

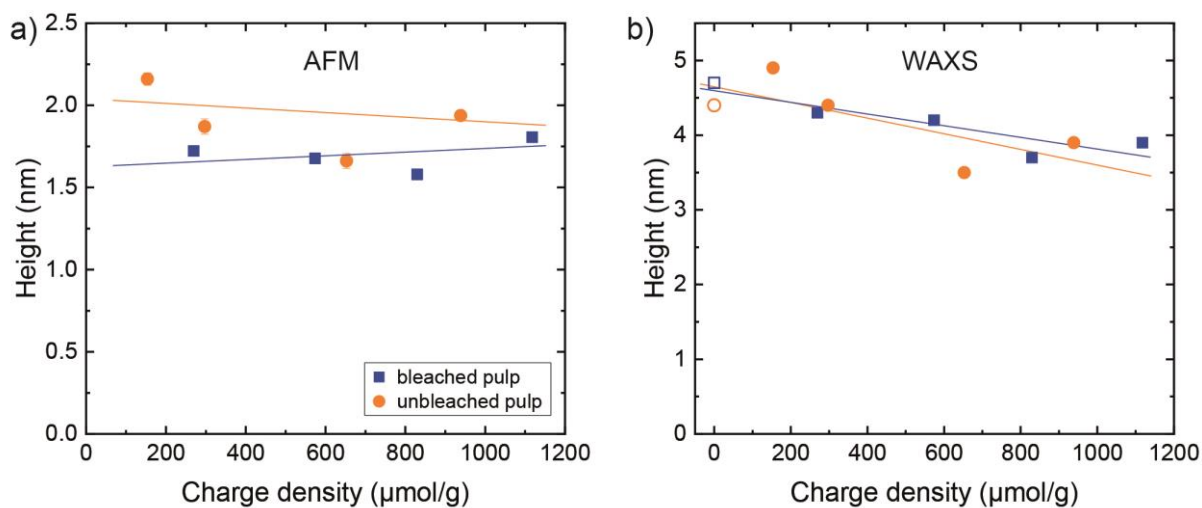


Figure S5. Average fibril height determined by a) AFM and b) WAXS as function of charge density. As zero charge density, WAXS measurements were done with unoxidized and unsonicated pulp (empty points), whereas the other points were done with lyophilized samples from sonicated fibril dispersions.

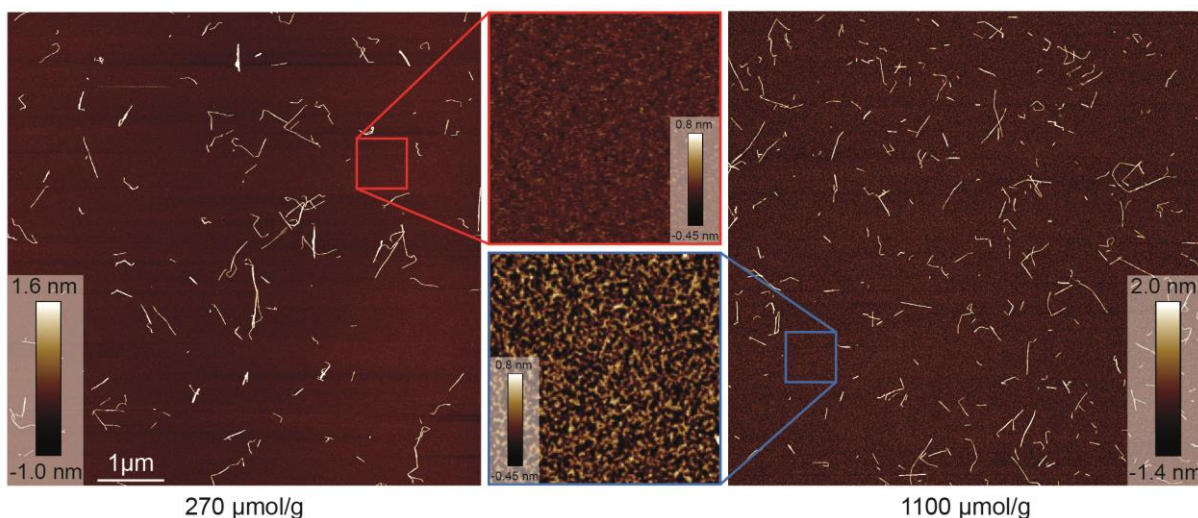


Figure S6. AFM images showing the difference in roughness of the APTES-modified mica surface while adsorbing CNF dispersions with low and high charge density. The roughness is coming from negatively charged single cellulose polymer chains. This change in roughness influences the determination of the zero-level to measure the height with FiberApp.

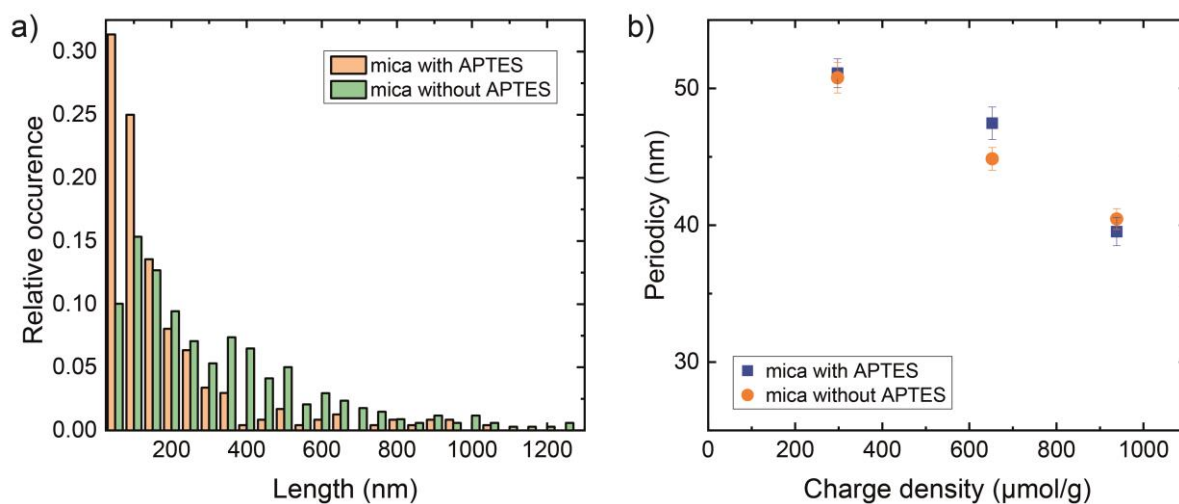


Figure S7. a) Histogram of length distribution of tracked fibrils on APTES-modified (orange) and unmodified (green) mica (CNF after 11 min sonication from the unbleached pulp treated with 10 mmol NaClO per gram cellulose). b) Comparison of twist periodicity of different charge density on APTES-modified (blue) and unmodified (orange) mica.

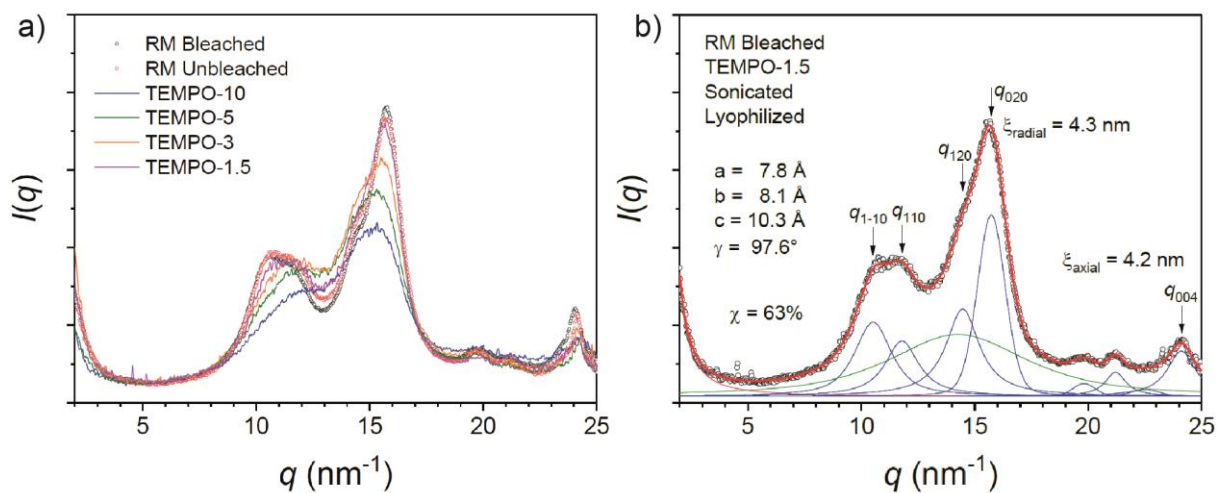


Figure S8. a) WAXS intensity profile of lyophilized bleached and unbleached industrial pulp and four bleached TEMPO-mediated oxidized samples (sonicated and lyophilized). b) Deconvolution of the WAXS profile of bleached CNF after sonication and lyophilization.

Supplementary table

Table S1. Parameters obtained from AFM image analysis and DLS for all different CNF samples.

Sample name*	Mean length (nm)	stdD	stdE	Length weighted length (nm)	stdD	stdE	Mean length (nm, DLS)	Inverse kink density	Average segment length (nm)	Number of kinks per fibril	Charge density ($\mu\text{mol/g}$)
1.5bl 05min	281	336	27	680	523	43		180	110	1.56	270
1.5bl 07min	332	336	23	671	478	33		177	116	1.87	270
1.5bl 11min	342	293	20	592	386	27		181	118	1.89	270
1.5bl 17min	313	279	27	560	374	36		183	116	1.71	270
1.5bl 25min	323	258	18	528	330	23		191	120	1.69	270
3bl 05min	352	359	31	715	511	44		228	138	1.54	570
3bl 07min	265	309	22	623	473	34	548	247	128	1.07	570
3bl 11min	292	283	11	567	395	15	422	239	132	1.22	570
3bl 17min	300	275	16	551	373	21	325	248	136	1.21	570
3bl 25min	327	266	10	544	343	13	329	234	136	1.40	570
5bl 05min	212	216	16	431	308	23		282	121	0.75	830
5bl 07min	255	248	14	496	346	19	231	231	121	1.10	830
5bl 11min	272	242	14	486	323	19	473	257	132	1.06	830
5bl 17min	285	233	7	476	301	9	347	286	143	1.00	830
5bl 25min	223	183	10	373	237	13	236	223	111	1.00	830
10bl 05min	234	191	18	388	245	23		254	122	0.92	1100
10bl 07min	205	168	9	342	217	12	343	321	125	0.64	1100
10bl 11min	204	166	8	339	214	10	403	340	127	0.60	1100
10bl 17min	185	160	6	323	212	8	338	349	121	0.53	1100
10bl 25min	199	145	6	304	180	8	189	343	126	0.58	1100
1.5ubl 05min	518	550	47	1098	800	69		193	141	2.69	150
1.5ubl 07min	493	441	30	885	590	40		207	146	2.38	150
1.5ubl 11min	468	380	32	774	489	41		216	148	2.17	150
1.5ubl 17min	447	367	30	746	474	39		208	142	2.15	150
1.5ubl 25min	390	303	22	624	383	28		177	122	2.21	150
3ubl 05min	553	554	60	1101	782	84		292	191	1.90	230
3ubl 07min	547	480	27	966	637	36	375	325	204	1.68	230
3ubl 11min	454	408	23	819	548	31	340	253	163	1.79	230
3ubl 17min	439	354	25	723	454	33	346	277	170	1.58	230
3ubl 25min	385	263	15	564	318	18	259	236	146	1.63	230
5ubl 04min	552	638	50	1285	974	77		396	231	1.39	650
5ubl 05min	482	462	29	922	639	41		389	215	1.24	650
5ubl 07min	493	469	38	935	645	52	338	356	207	1.38	650
5ubl 11min	459	381	24	774	495	31	383	303	183	1.51	650
5ubl 17min	400	339	22	686	444	28	332	321	178	1.25	650
5ubl 25min	335	255	13	529	321	16	215	320	164	1.05	650
10ubl 05min	329	315	26	628	435	36		323	163	1.02	940
10ubl 07min	294	230	14	473	292	18	456	436	176	0.67	940
10ubl 11min	268	261	17	520	363	24	459	411	162	0.65	940
10ubl 17min	288	219	10	453	274	13	412	523	186	0.55	940
10ubl 25min	264	193	9	405	239	11	253	477	170	0.55	940

*The sample name is a compound from: amount of NaClO [mmol/g cellulose]; bleached (bl) or unbleached (ubl); sonication time, e.g. 3 bl 11min = 3 mmol NaClO per g cellulose, bleached pulp, 11 min sonication.

Table S2. Crystallinity data from WAXS deconvolution for different pulps and dispersions.

NaOH (mmol/g)	Crystallinity (%)				
	bleached			unbleached	
	sonicated	unsonicated		sonicate	unsonicated
	lyophilized	evaporated	lyophilized	lyophilized	lyophilized
0			66		68
1.5	63			64	
3	58	69	72	63	
5	62	66	65	67	
10	50	75	67	60	
Average	58		69	64	68

Table S3. Yield after sonication and centrifugation.

Sample name*	Yield (%)
10 bl, 11 min	0.86
10 ubl, 11 min	0.89
5 bl, 11 min	0.85
5 ubl, 11 min	0.84
3 bl, 11 min	0.35
3 ubl, 11 min	0.31
1.5 bl, 11 min	0.24
1.5 ubl, 11 min	-

*The sample name is a compound from: amount of NaClO [mmol/g cellulose]; bleached (bl) or unbleached (ubl); sonication time, e.g. 3 bl 11 min = 3 mmol NaClO per g cellulose, bleached pulp, 11 min sonication.

Supplementary material and methods

Materials and chemicals

If not stated otherwise, the chemicals were obtained by Sigma Aldrich and used without further purification. Bleached and unbleached never-dried sulphite softwood-dissolving pulp was obtained by Domsjö, Sweden. The degree of polymerization (DP) of both pulps was around 770, determined by Domsjö.

Instrument list

Ultra-sonicater:	Hielscher UP200S
DLS:	Zetasizer Nano ZS, Malvern Instruments Ltd. U.K.
Centrifuge:	Centrifuge 5810 R, Eppendorf Prism Microcentrifuge, Labnet Sigma 3K3OH, Sigma
Charge density:	Conductivity meter EL30/EL3, Mettler Toledo
AFM:	MultiMode VIII Scanning Probe Microscope, Bruker, USA
WAXS:	Rigaku MicroMax-002 ⁺ , Rigaku Innovative Technologies, Auburn Hills, Michigan, USA