Supporting Information

Cellulose nanomaterial metrology: microscopy measurements

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Table 1. Particle size measurements for CNCs using imaging methods. Industrial sources are noted by company name and lab synthesized materials are noted with brief details on cellulose source and surface chemistry (sulfated vs carboxylated). If not noted, the samples were generated from wood pulp using sulfuric acid, giving sulfate half ester groups on the surface. References numbers are from the review.

Sample source	Method	Length, distribution breadth (nm)[1]	Cross section, distribution breadth (nm)[1]	Number of particles	Refer-ence
Lab made (various conditions)	TEM	130.5 to 281.2 (9 samples)	nd	50-350	65
CelluForce CNC	AFM-1[2]	91.0, 32.4	4.19, 1.17	300	34
CelluForce CNC	AFM-2[2]	87.6, 28.4	4.35, 1.30	285	34
CelluForce CNC	TEM-1[2]	66.5, 26.5	8.0, 1.8	411	34
CelluForce CNC	TEM-2[2]	75.2, 26.9	7.1, 1.5	287	34
Lab made (sulfated)	AFM	nd	4.0, 0.34[3]	300	69
Lab made (sulfated)	TEM	163, 0.426[3]	nd	250	69
Innventia AB (carboxylated)	AFM	nd	3.2, 0.35	300	69
Innventia AB (carboxylated)	TEM	328, 0.42	nd	250	69
Lab made (bacterial cellulose)	AFM	520	6.7, 2.5	>1000 (height)	55
Lab made (carboxymethylated)	AFM	310	5.0, 2.0	>1000 (height)	55
Lab made (sulfated)	AFM	200	7.0, 2.7	>1000 (height)	55
CNCD-1[4]	AFM-1[2]	76, 32	3.4, 1.1	1567	15
CNCD-1[4]	AFM-2[2]	78, 30	3.7, 1.2	1546	
CNCD-1[4]	TEM-1[5]	82, 36	7.5, 2	1909	15
CNCD-1[4]	TEM-2[5]	92, 33	7.2, 1.6	600	
Lab made (wood, sulfated)	AFM	116, 67	nd	250-300	54
Lab made (cotton, sulfated)	AFM	130, 60	nd	250-300	54
CNCD-1[4]	AFM	nd	3.5, 1.1	321	70
CNCD-1[4]	AFM	94.5, 39.6	3.44, 1.21	ILC data[6]	50
CNCD-1[4]	TEM	95.8, 39.0	7.65, 2.20	ILC data[6]	64
Lab made (filter paper)	AFM	132, 55	8, 3	≥ 100	53
CelluForce	AFM	183, 88	6, 2	≥ 100	53
Alberta Innovates	AFM	134 56	8, 2	≥ 100	53
Forest Products Lab	AFM	134, 52	7, 2	≥ 100	53
Lab made (filter paper	AFM	190, 40	8, 2	100	52
Noram	AFM	160, 30	5, 1	100	52
Melodea	AFM	210, 60	4, 1	100	52
Anomera	AFM	150, 30	5, 2	100	52
Blue Goose Biorefineries	AFM	210, 50	5, 2	100	52

CelluForce CNC	AFM	118.1, 45.9	4.3, 1.5	nd	66
CelluForce CNC	TEM	141.5, 60.0	12.8, 3.1	nd	66
U Maine CNC	AFM	101.1, 34.4	4.9, 1.7	nd	66
U Maine CNC	TEM	88.9, 37.5	6.2, 1.6	nd	66
CelluForce (20 kJ/g/L sonication energy)	AFM	nd	4.8, 0.1	> 139	40
CelluForce (3063 kJ/g/L sonication energy)	AFM	nd	4.4, 0.1	> 139	40
Lab made (cotton, sulfated)	AFM	189, 0.31[3]	6.8, 0.18[3]	≥ 100	58
Lab made (cotton, carboxylated)	AFM	277, 0.27[3]	8.0, 0.34[3]	≥ 100	58
Lab made (cotton-sulfate, carboxyl)	AFM	203, 0.27[3]	7.8, 0.38[3]	≥ 100	58
Bacterial CNC-batch 1	AFM	382, 0.36[3]	6.9, 0.27[3]	≥ 100	58
Bacterial CNC-batch 2	AFM	370, 0.41[3]	7.8, 0.38[3]	≥ 100	58

[1]Data are presented as mean and standard deviation as a measure of distribution breadth, unless otherwise noted. Cross section is the measured width for TEM and the measured height for AFM unless otherwise noted. Cases where data was not measured or not reported are indicated by "nd".

[2] data obtained by two analysts for a single data set

[3] data are mean and polydispersity obtained for a log normal fit of data

[4] CNCD-1 is a certified reference material characterized and released by NRC and obtained from CelluForce

[5] TEM data for 2 different laboratories

[6] ILC data is presented as the overall consensus value obtained from data from 10 laboratories all measuring samples prepared in a single laboratory. The number of particles analyzed varies from 355 to 620 for AFM (with one exception of 125 particles) and from 232 to 1179 for TEM. Overdispersion vales which provide a measure of uncertainty in the measurement are 15 nm and 0.28 nm (AFM length, height) and 12.3 nm and 0.78 nm (TEM length, width).

Table 2. Particle size measurements for iCNFs using imaging methods. Samples are all prepared by TEMPO-mediated oxidation of wood pulp (carboxylated) in the authors' laboratory unless otherwise noted. Details on differences in sample preparation (surface charge, sonication) are provided for some samples. References numbers are from the review.

Sample source	Method	Length, distribution breadth (nm)[1]	Cross section, distribution breadth (nm)[1]	Number of particles	Reference
iCNF	AFM	511, 0.77[2]	2.35	2380	29
iCNF	AFM-		2.0, 0.6	100	16
iCNF	AFM		2.2, 0.8	100	16
iCNF	AFM		2.9, 0.9	100	16
iCNF (low charge)	AFM	3900	3.3, 1.2	>1000 (length)	55
iCNF (high charge	AFM	860	3.3, 1.2	>1000 (length)	55
iCNF (carboxy-methylation)	AFM	1700	2.9, 1.2	>1000 (length)	55
iCNF	AFM	800, 376	18.5, 4.5[3]	100 (length) 50 (width)	81
iCNF (deinked paper)	AFM	724, 391	20, 6.1[3]	100 (length) 50 (width)	81
iCNF (380 µmol/g)[4]	TEM	614		~200	77
iCNF (1360 µmol/g)[4]	TEM	419		~200	77
iCNF (380 µmol/g)[4]	AFM		2.14	~150	77
iCNF (1360 µmol/g)[4]	AFM		2.47	~150	77
iCNF (8 samples, varying fibrillation)	AFM		2.4 – 2.6 nm	~50	76
iCNF (total length)	AFM	1300 (0 s sonication) 400 (400 s sonication)[5]		240	80
iCNF (segment length)	AFM	300 (0 s sonication 150 (400 s sonication)[5]		240	80
iCNF (150 µmol/g)[4]	AFM	493		>200	79
iCNF (650 µmol/g)[4] 5 min sonication	AFM	482		>200	79
iCNF (650 µmol/g)[4] 25 min sonication	AFM	335		>200	79
iCNF (940 µmol/g)[4]	AFM	294		>200	79
Tunicate CNF	AFM[6]		3.0, 1.5[6] 7.4, 2.0 13.0, 2.9		75

[1]Data are presented as mean and standard deviation as a measure of distribution breadth, unless otherwise noted. Cross section is the measured height for AFM unless otherwise noted

[2]Polydispersity from log normal fit
[3] AFM width, no deconvolution
[4] Charge density in brackets
[5] Data estimated from graph
[6] Three component fit

Table 3. Particle size measurements for CNFs using imaging methods. Brief descriptions of the sample preparation conditions are included; see references for additional details. References numbers are from the review.

CNF sample source	Method	Length, distribution breadth (μm)[1]	Cross section, distribution breadth (nm)[1]	Number of particles	Reference
Bleaching, grinding of carrot agricultural waste	AFM[2]		12, 8	40	98
Bleaching, grinding of beer production waste	AFM-		30, 13	40	98
Birch pulp, fluidizer, centrifugation 3 processing conditions	AFM[3]		4.2, 2.7 5.6, 3.2 19.5, 13.2	505 523 631	88
Softwood bleached Kraft fiber, grinder (2 samples)	SEM	CNF-50: 6.7, 5.6 CNF-80: 6.8, 4.7	CNF-50: 64, 29 CNF-80: 85, 40.5	101 92	90
Softwood bleached Kraft fiber, grinder (2 samples)	TEM[4]	nd	49.92, 43.69 83.23, 57.02	nd	90
Bleached birch pulp; 6 passes of fluidizer	AFM[5]		Height: 6, 3 Width: 67, 18	500	87
Bleached birch pulp; 6 passes of fluidizer	Negative contrast SEM	1.46, 0.8	35, 12	200	87
Bleached eucalyptus pulp, mechanically refined, 1 or 3 homogenization passes[6]	FEG-SEM		53, 85 (one pass) 12, 15 (three passes)	899 4723	94
Eucalyptus pulp, mill refined and homogenized (two samples) [6]	FEG-SEM		26, 27 (less processed) 17, 15 (more processed)	2946 4723	86
CNF from aqueous counter collision using bacteria (a), hardwood (b) and microcrystalline cellulose (c)	AFM	4.0, 2.3 (a) 4.2, 2.4 (b) 2.5, 1.7 (c)		nd	99
Bleached softwood pulp; supermass collider	FE-SEM	1.2, 0.4	38.8, 14.8	nd	97

[1]Data are presented as mean and standard deviation as a measure of distribution breadth, unless otherwise noted. Cross section is the measured height for AFM or the measured width for TEM/SEM, unless otherwise noted. Studies lacking some data or particle number information are noted as "nd".

[2] SEM length histograms shown but no quantitative data

[3] fractionated by sequential centrifugation to give three samples with differing fibril sizes

[4] Node to node length and number of branches per node were also measured; see text in CNF section
[5] AFM data is for CNF on a polymer-coated mica. The width decreases for CNF after deconvolution and when deposited on bare mica but in both cases is still larger than the measured height .
[6] Additional data on other sample preparation and image collection conditions and median, skewness, etc for particle diameter distributions are available in references 86 and 94.