

Supplementary information

Expandable and scalable production of cellulose nanofibrils *via* highly efficient swelling-modification in deep eutectic solvent

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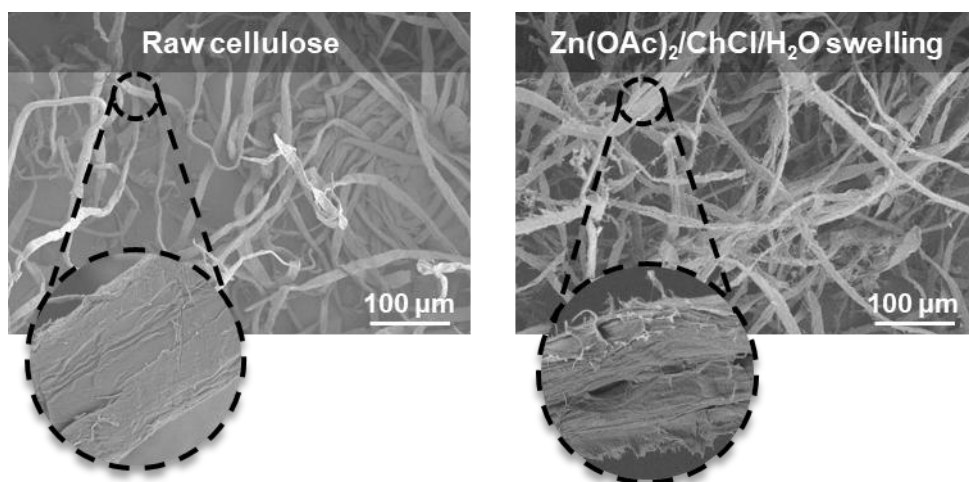
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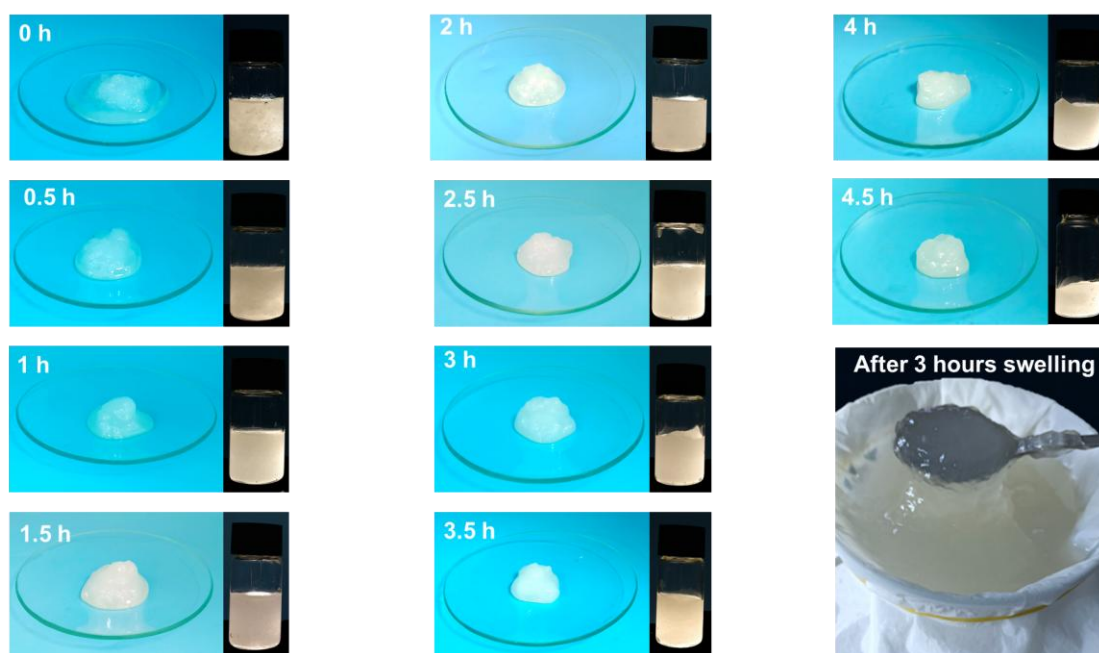
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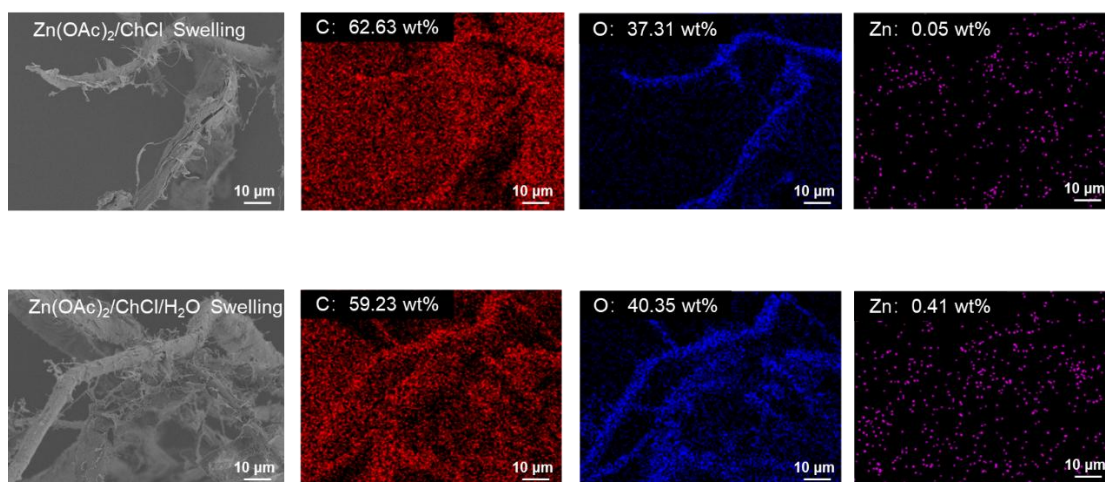
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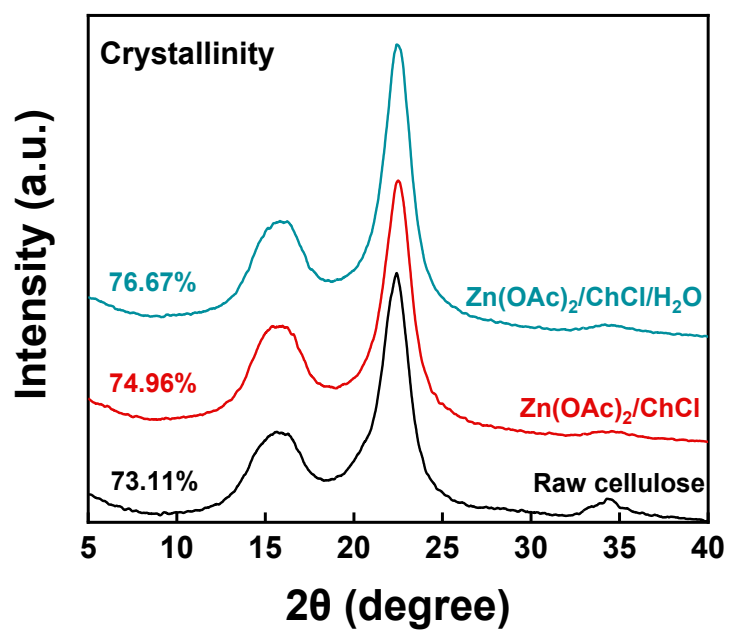
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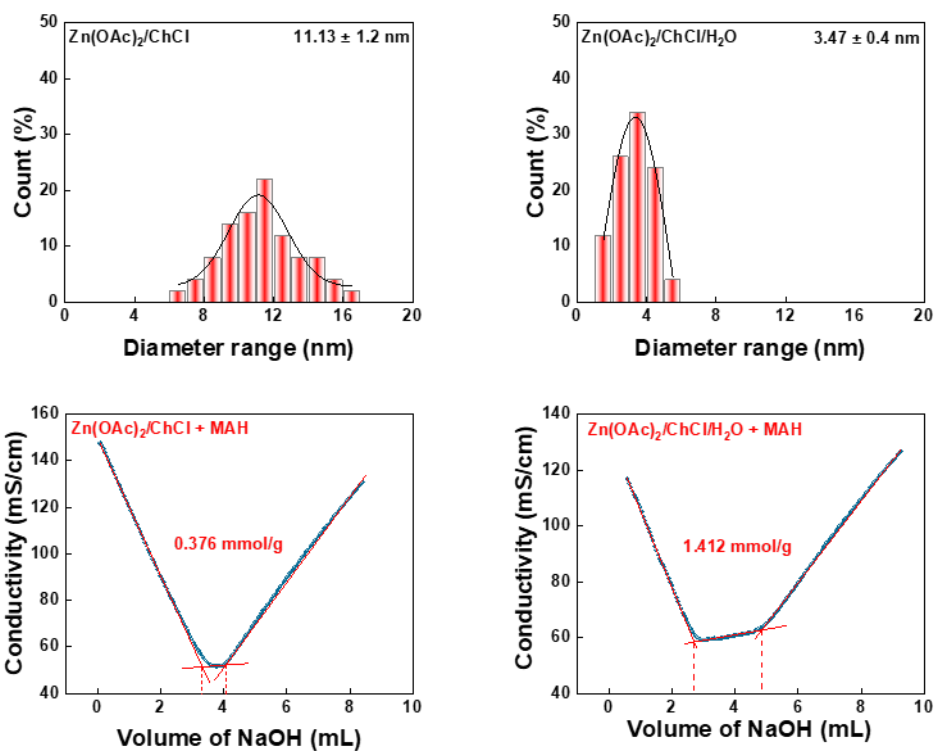
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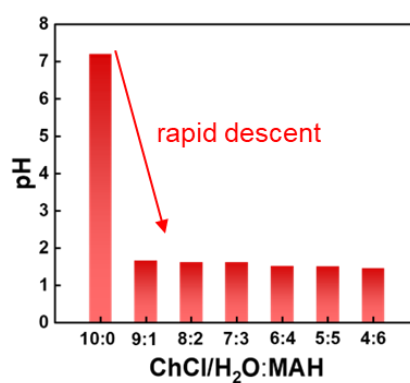
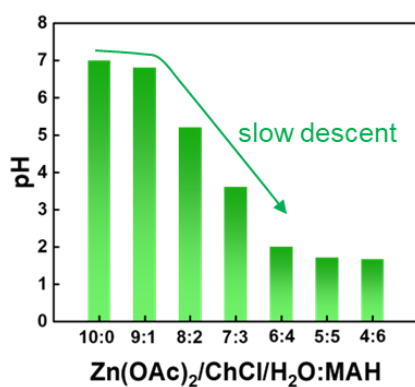
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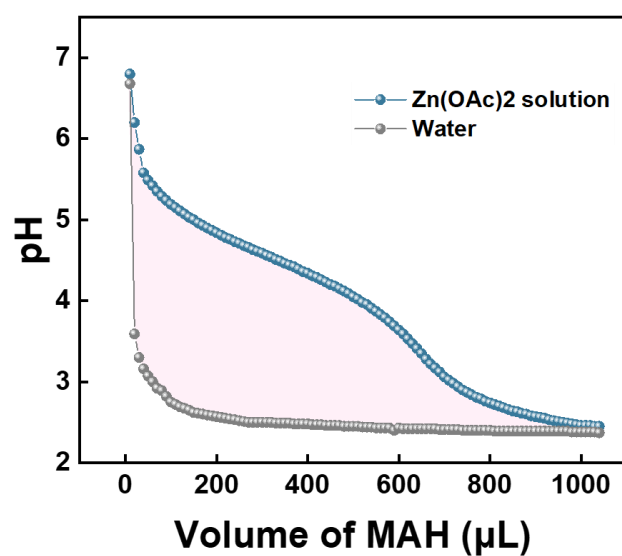
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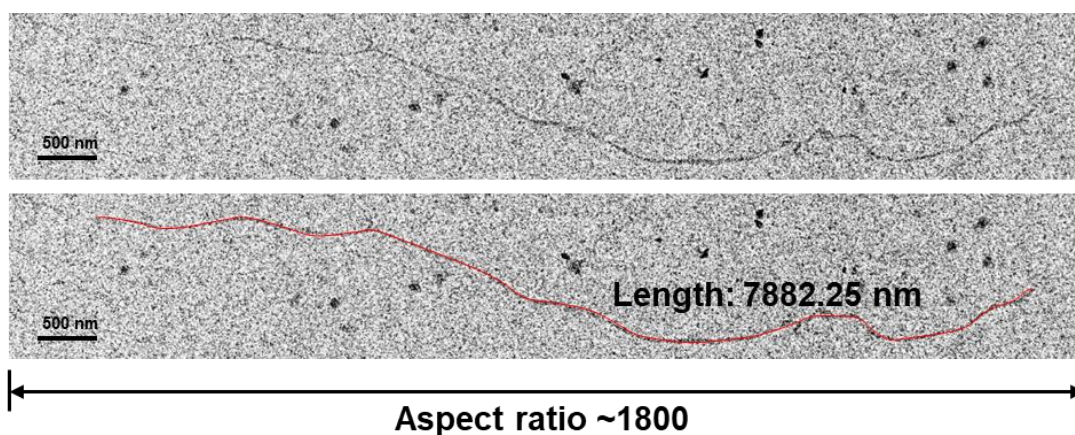
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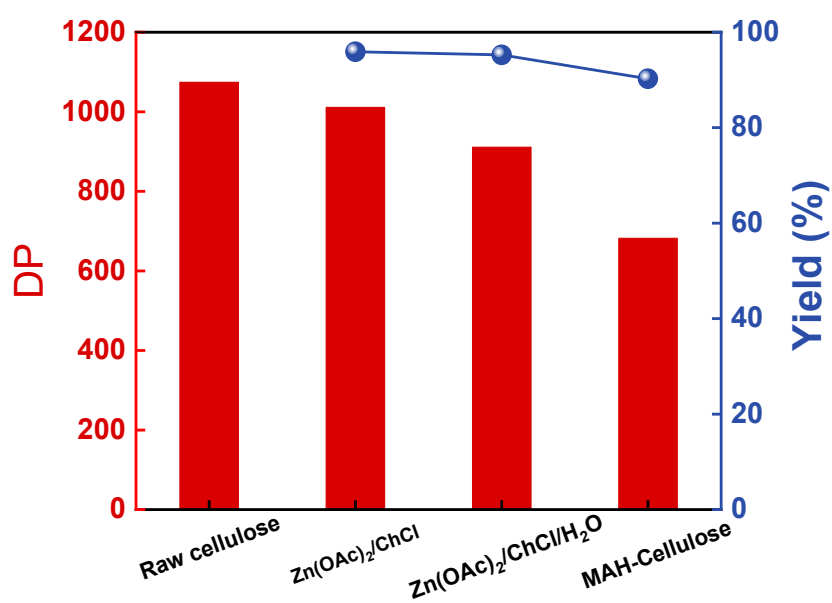
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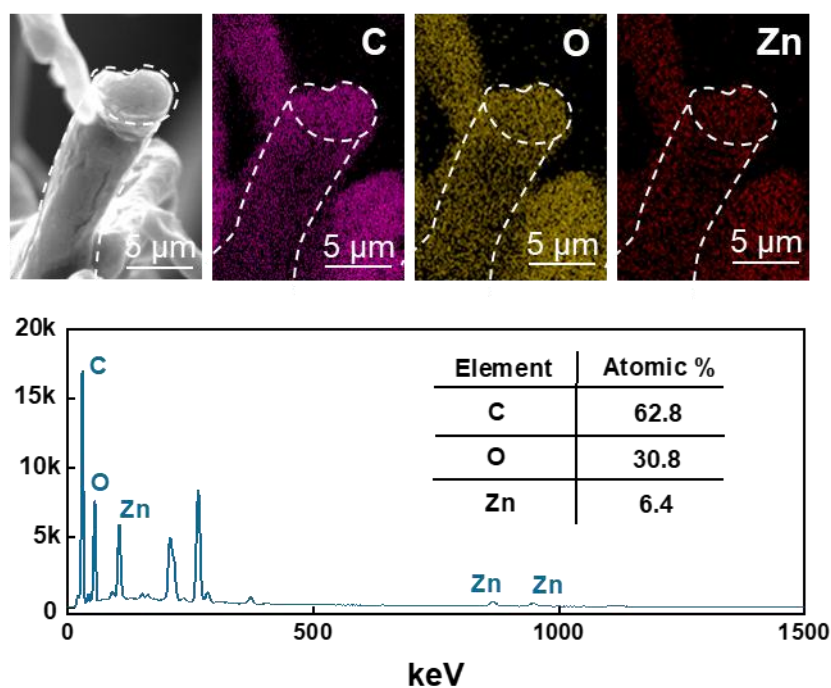
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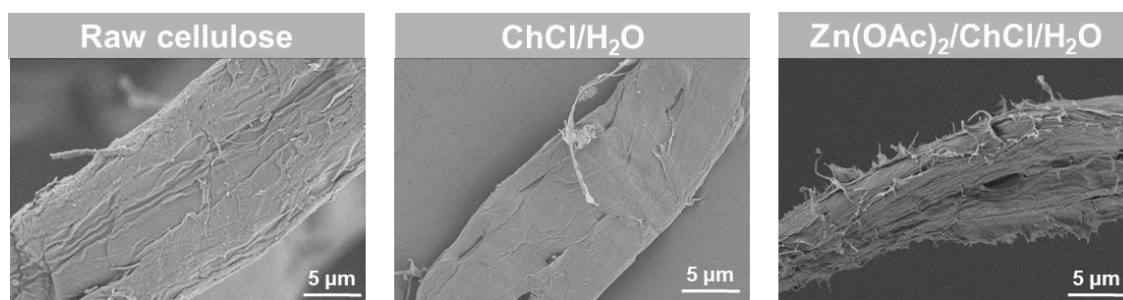
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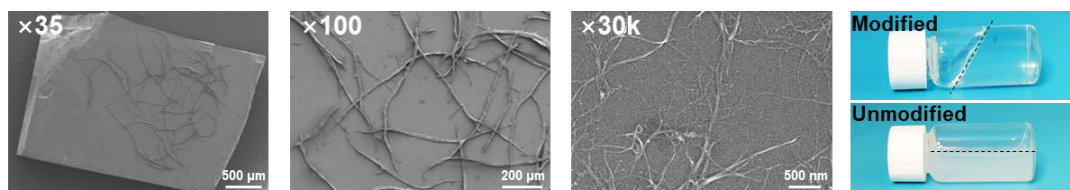


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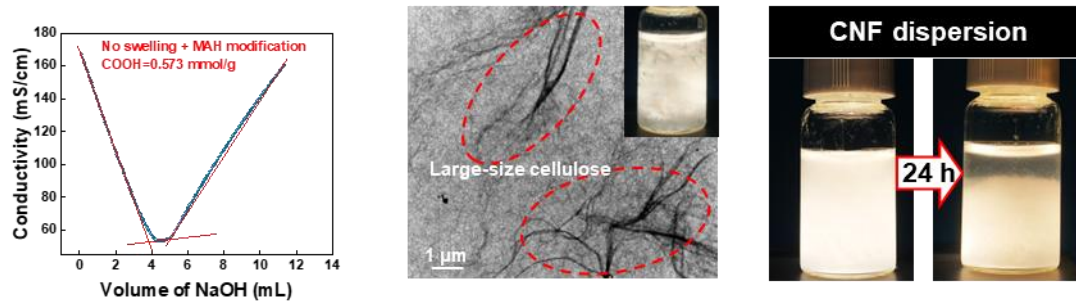
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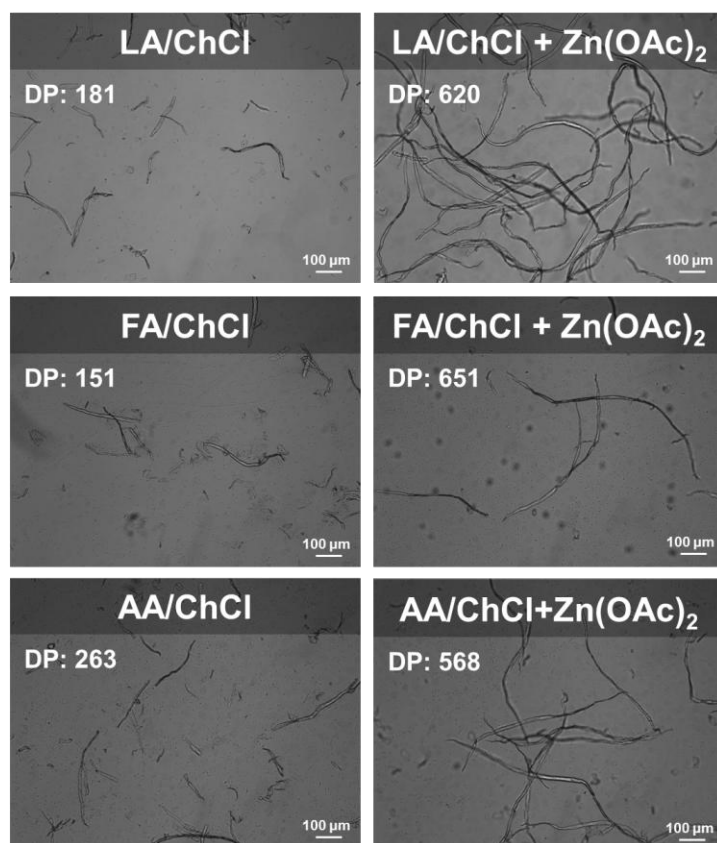
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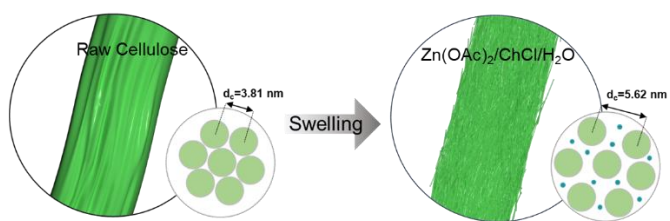
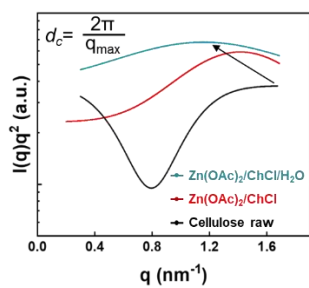
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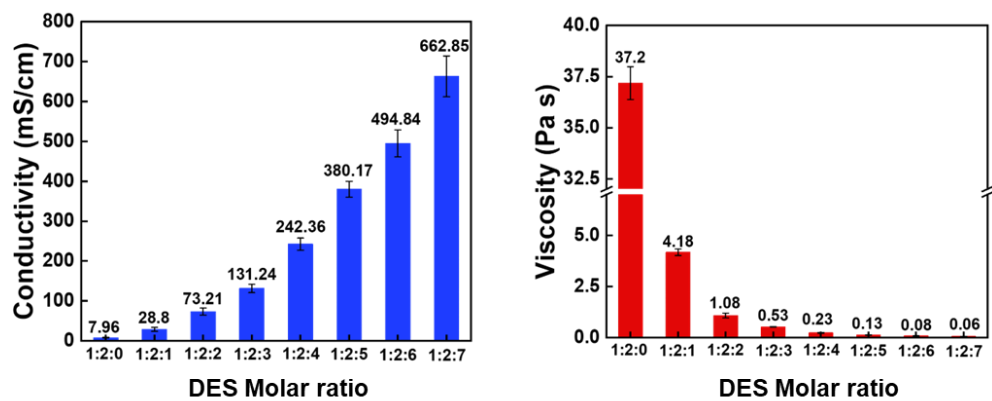
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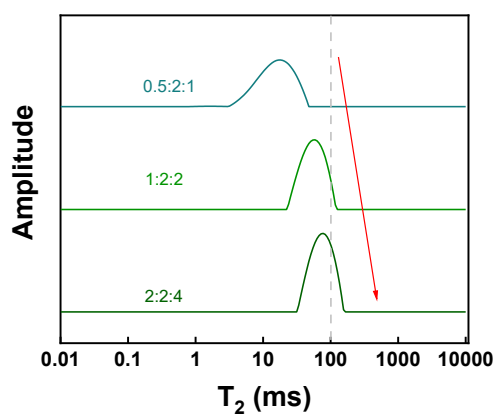


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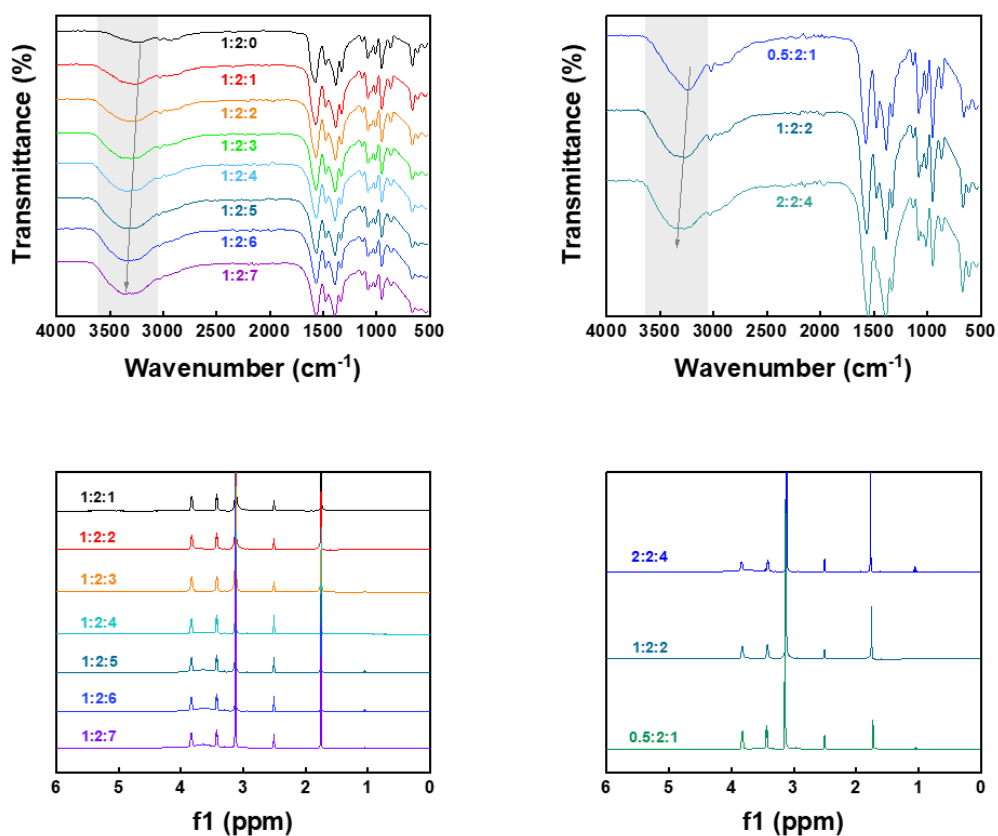
Values represent the means $\pm$ SD from n=3 independent samples.



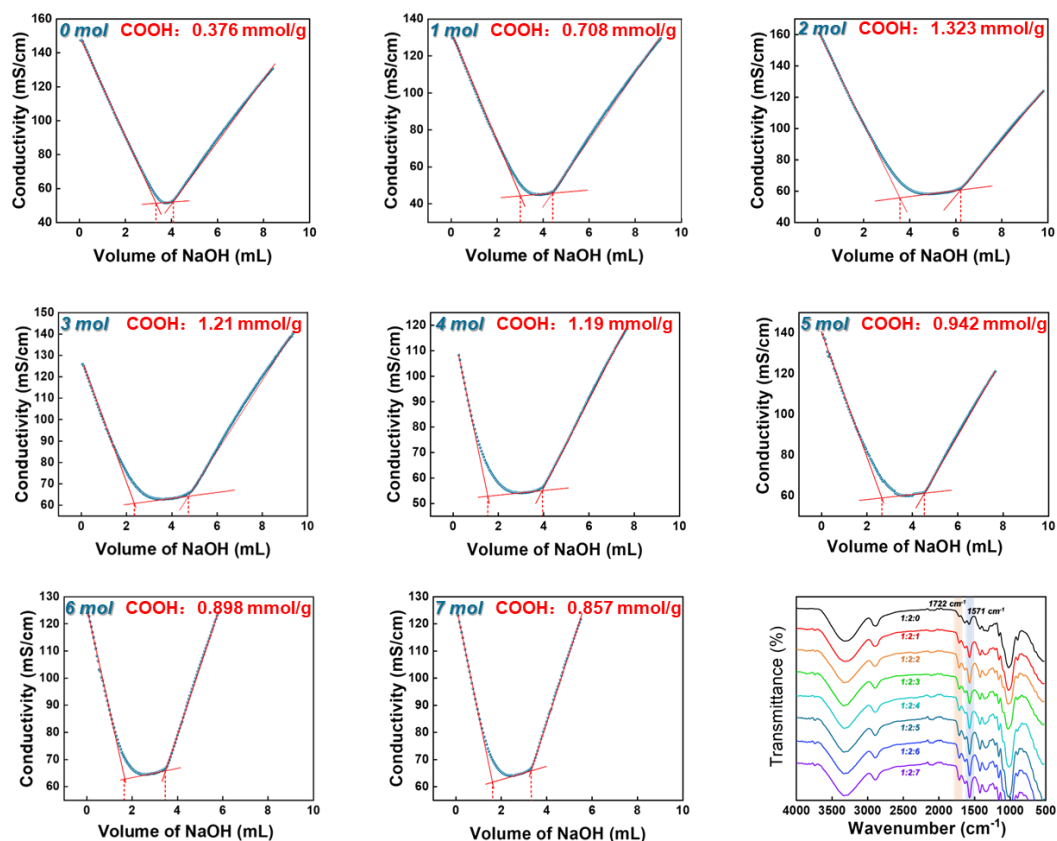
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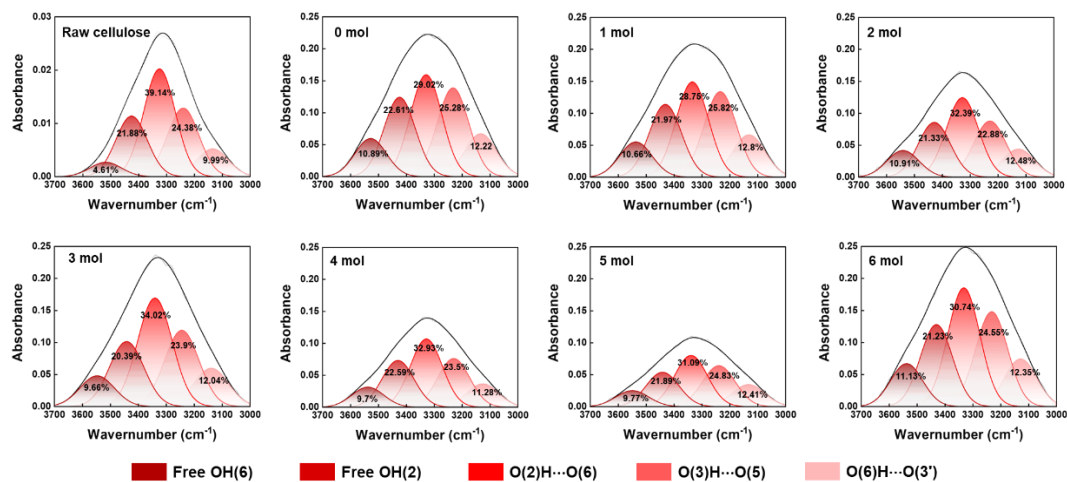
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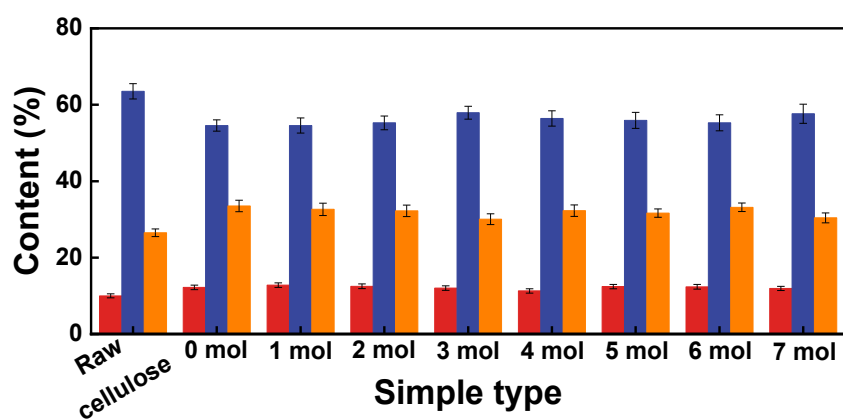
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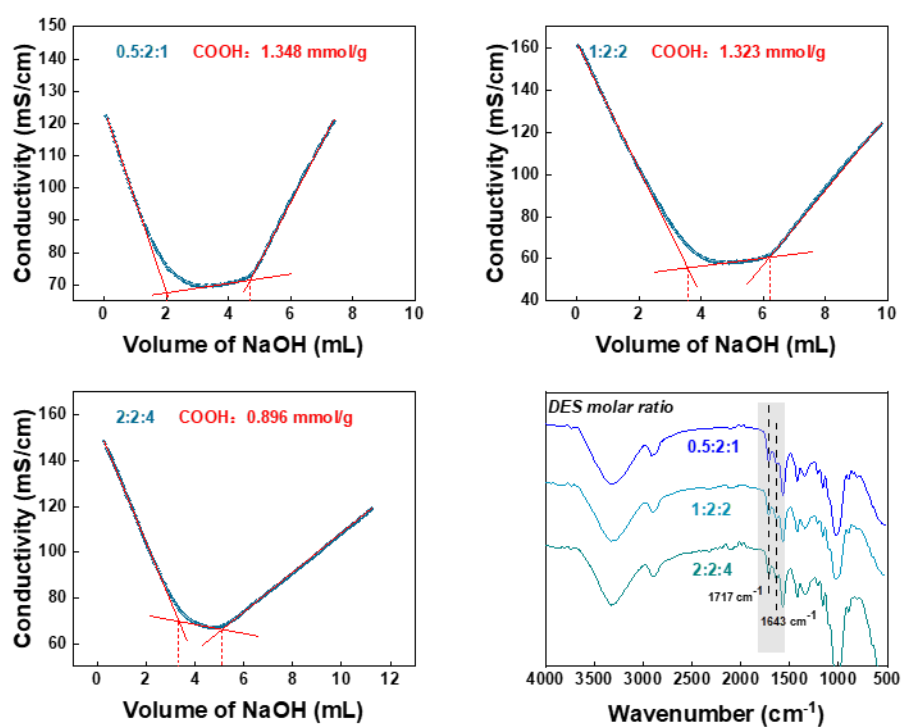


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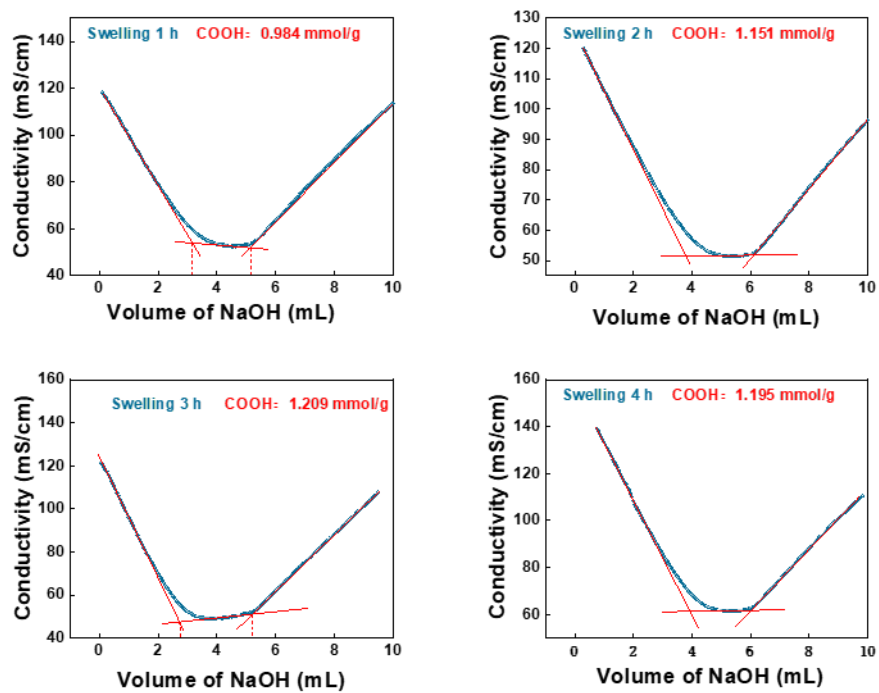


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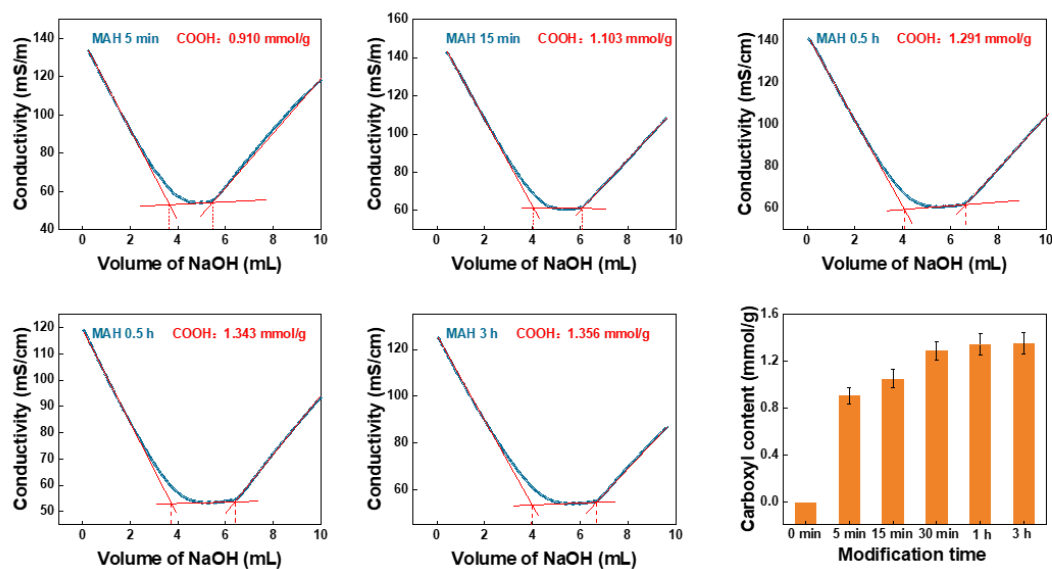
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 161 Values represent the means $\pm$ SD from n=3 independent samples.



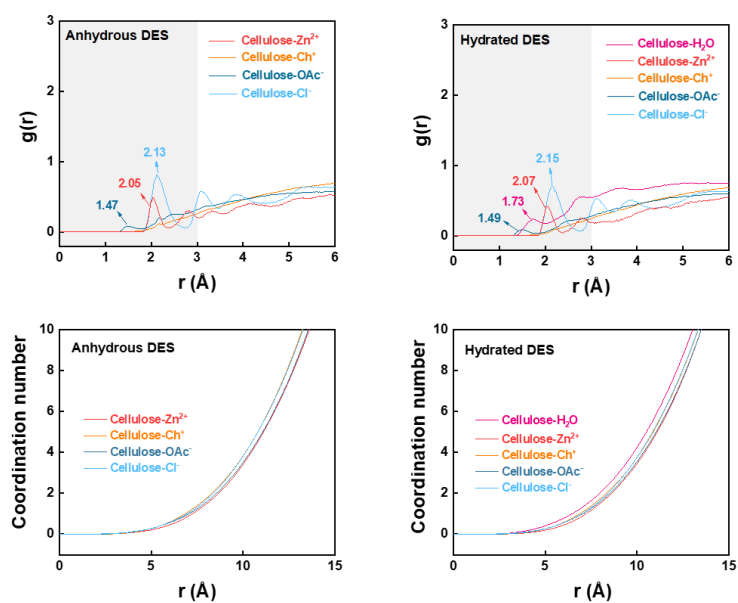
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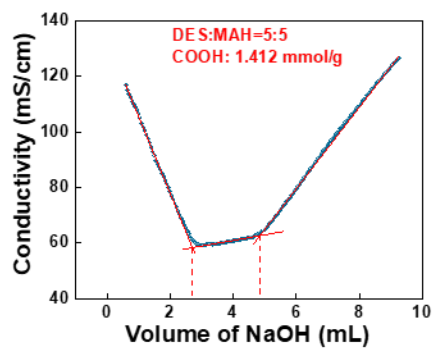
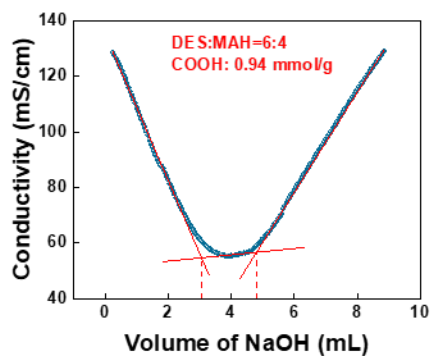
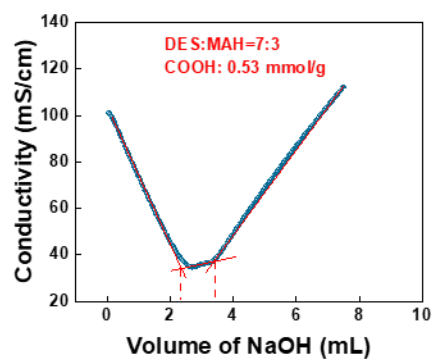
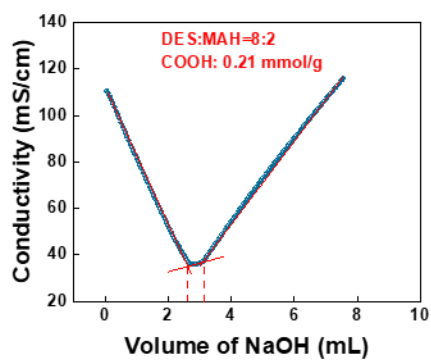
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Supplementary Fig. S25. Relationship between MAH modification time and carboxyl content of CNFs under the optimal DES swelling condition (1:2:2). Values in m represent their means $\pm$ SDs from n=3 independent samples. Values represent their means $\pm$ SDs from n=3 independent samples.

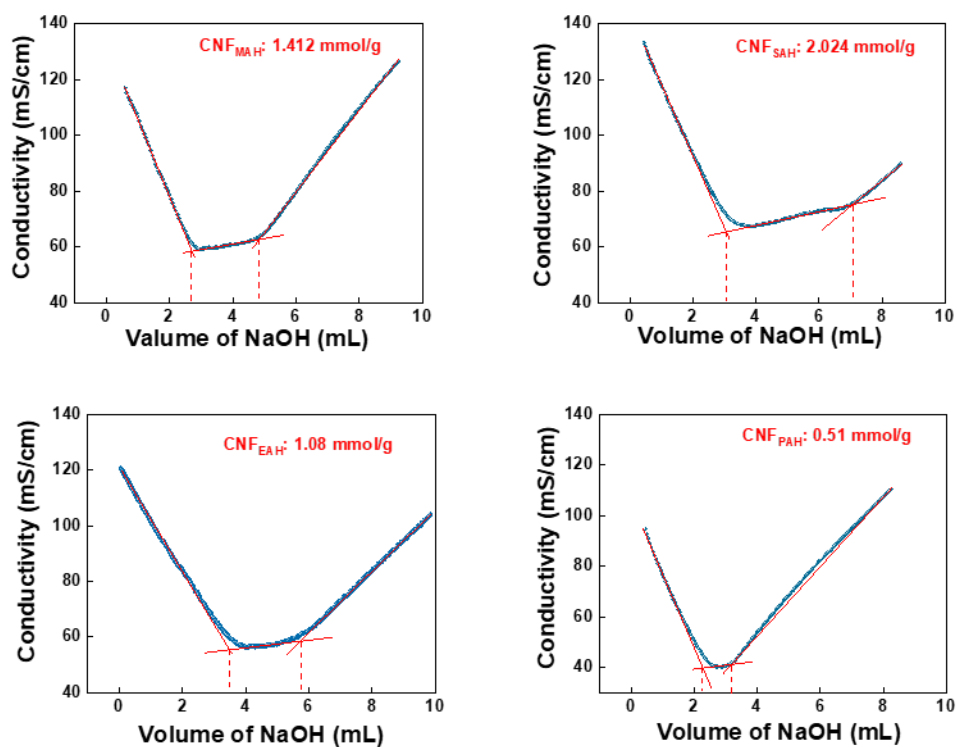


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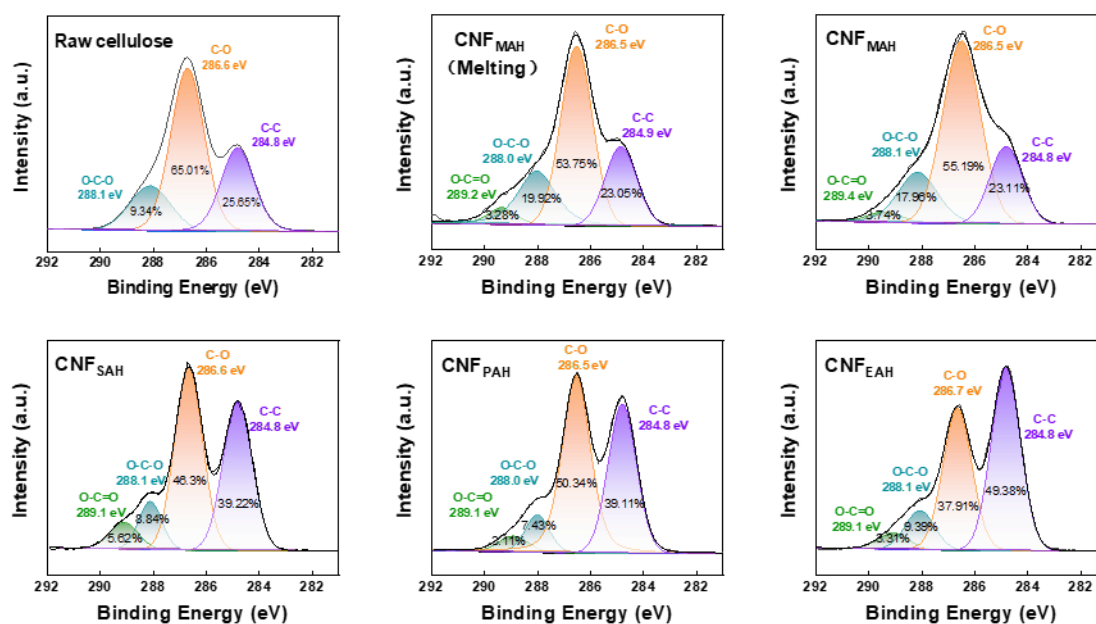


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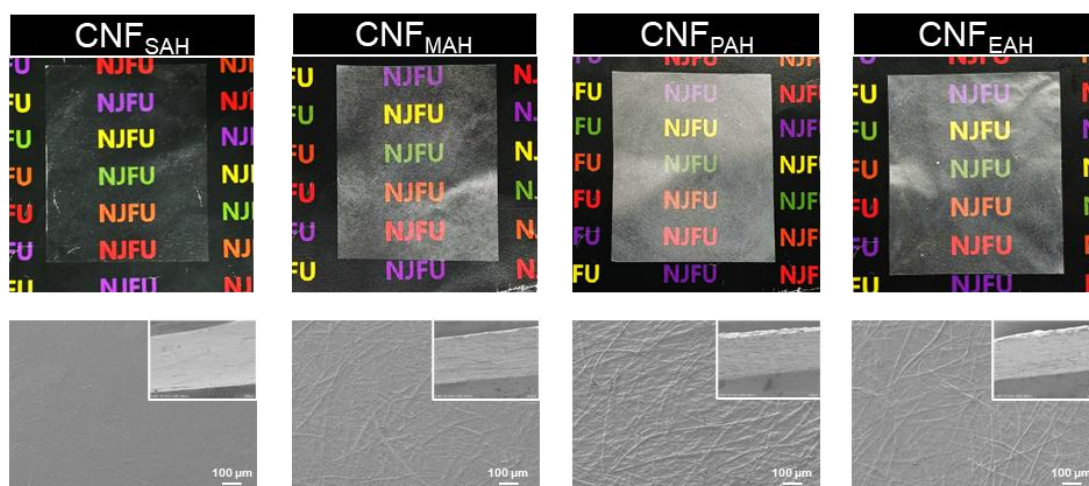
178 **Supplementary Fig. S27.** Effect of modified DES with different MAH and DES ratios
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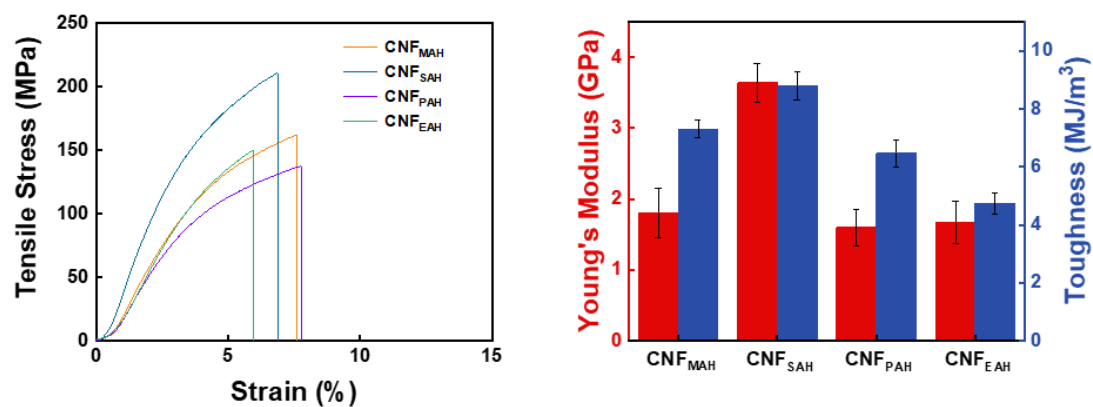
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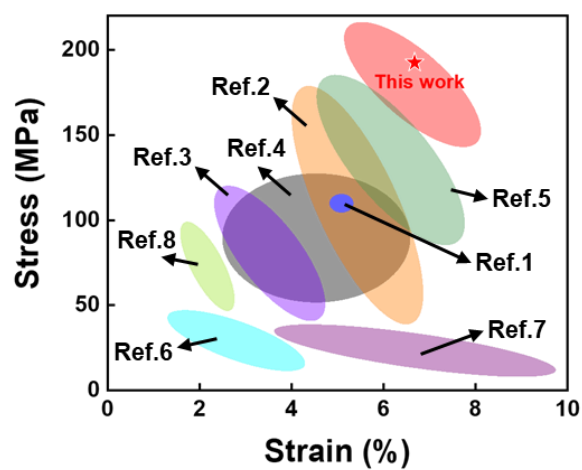
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Supplementary Fig. S30. Digital photographs and SEM micrographs of films from the four expandable functionalized CNFs.

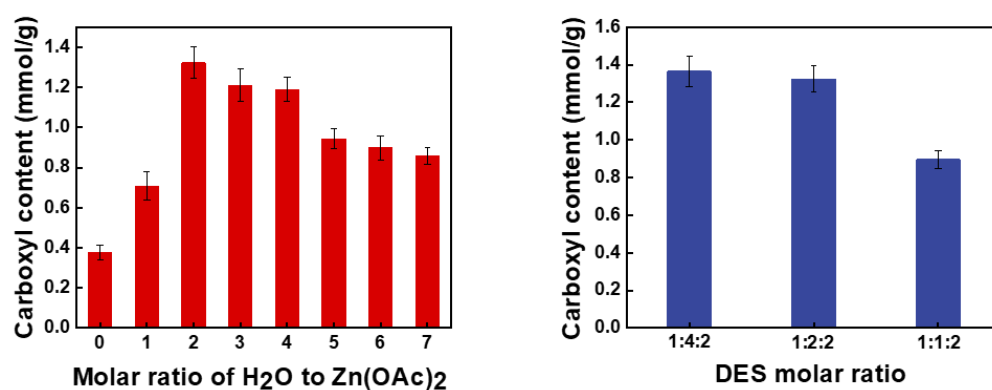


Supplementary Fig. S31. Stress-strain curves of films from the four expandable functionalized CNFs, including calculated Young's modulus and toughness. Values represent the means $\pm$ SDs from $n=3$ independent samples.



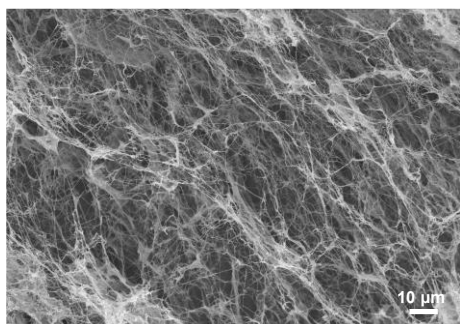
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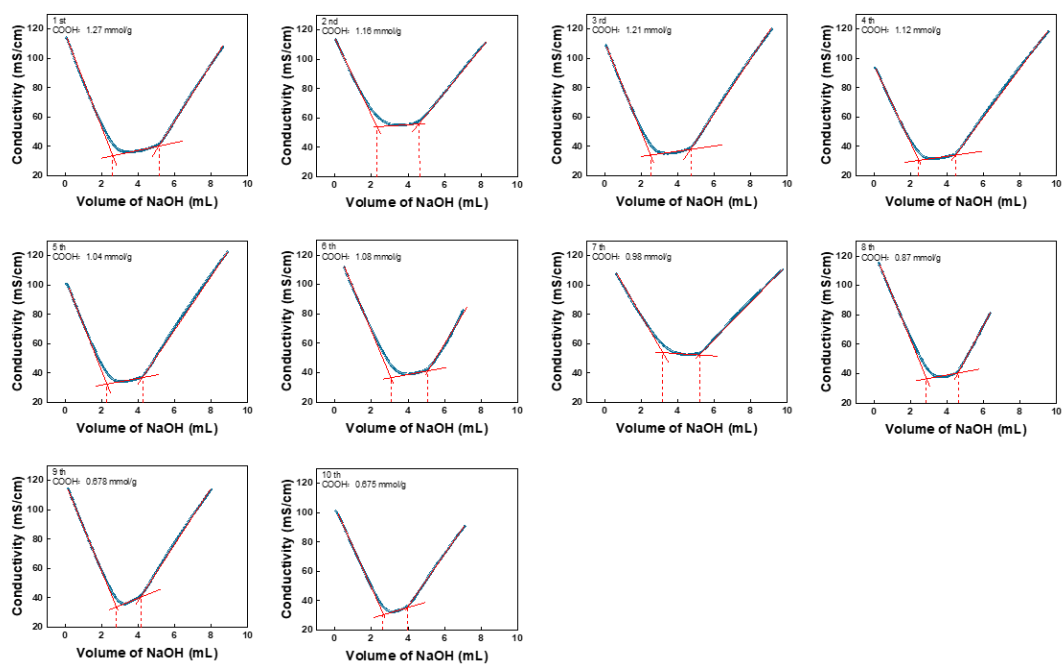
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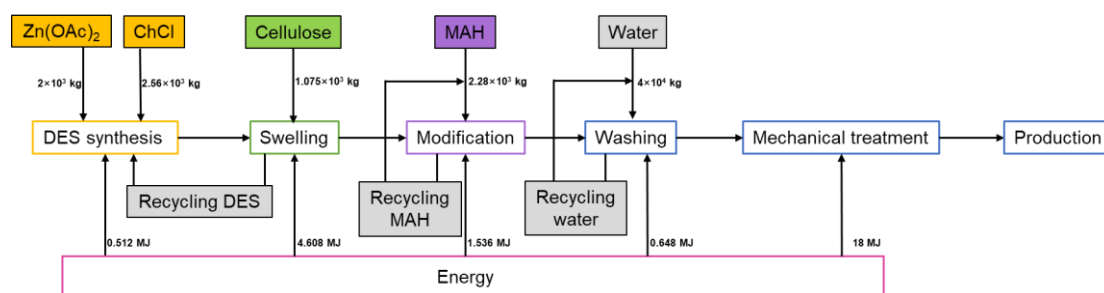
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201 **Supplementary Fig. S34.** SEM images and digital photographs of CNF_{MAH},

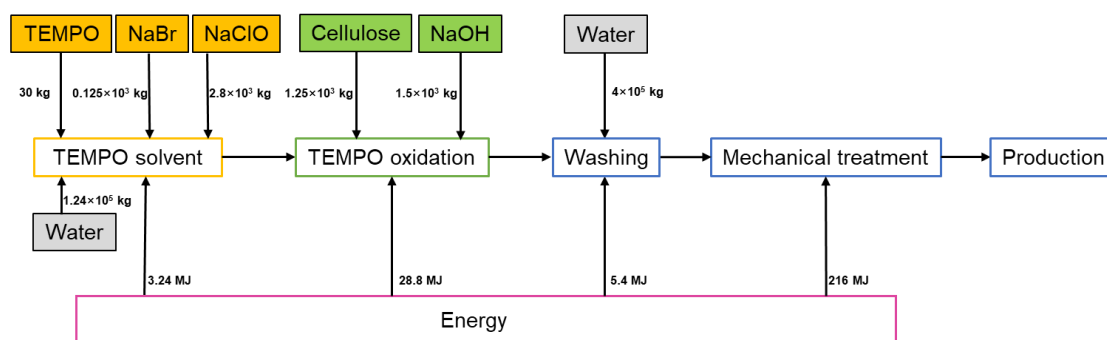
202 highlighting the birefringence phenomenon.



Supplementary Fig. S35. Carboxyl content of CNF_{MAH} over 10 cycles of DES exposure.



Supplementary Fig. S36. Network diagram illustrating the production of DES-based CNFs.



Supplementary Fig. S37. Network diagram showing the production of CNF by the TEMPO oxidation method.

212 **Supplementary Table S1.** Comparison of different preparation methods for CNFs and their corresponding data.

Type	COOH (mmol/g)	Diameter (nm)	Length (μm)	Aspect ratio	Yield (%)	DP	Cycle	Ref.
Zn(OAc) ₂ /ChCl/H ₂ O+SAH	2.024	3.61	5-8	1800	90-93	690	10	Our work
Zn(OAc) ₂ /ChCl/H ₂ O+MAH	1.412	3.72		1800		680		
Zn(OAc) ₂ /ChCl/H ₂ O+EAH	1.08	4.52		1200		730	-	
Zn(OAc) ₂ /ChCl/H ₂ O+PAH	0.51	5.19		900		780		
TOCN	1.5	4	0.87	217	82	-	-	1
TOCN	1.25	4	0.93	233	20-65	380		2
TOCN	1.74	3.5	0.23	65	-	370		3
OA/ChCl/p-TA	0.43	5.9	0.5	85	6			4
OA/ChCl	0.29	6.9	0.35	50	39			4
OA/ChCl/AlCl ₃ ·6H ₂ O	0.74	15.34	0.475	31	56			5
CA/ChCl	1.5	3.4	10.4	2500	90.12		10	6
OA/ChCl	0.27	15.7	0.337	21	76			7
OA/ChCl/FeCl ₃ ·6H ₂ O	0.2	5-20	0.05-0.3		72		3	8
CA/ChCl	0.31	8			76			9
OA/ChCl	0.12-0.17	4-34		5.1-7.9	14-33	223-282	5	10
MAH	1.6	5		390	95			11
Sulfamic acid/Glycerol	0.18-0.7	10-25			80-95	412-638		12
Cyclic anhydride	0.5-1.2	3-5		1400	98			13

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214 **Supplementary Table S2.** Hydrogen bond parameters of CNFs swollen with DES at
 215 varying water contents.

Simple	H-bond	Wavenumber (cm ⁻¹)	Content (%)	R ²
HBKP	O(6)H...O(3')	3134.2	9.99	0.9986
	O(3)H...O(5)	3240.5	24.38	
	O(2)H...O(6)	3325.6	39.14	
	Free OH(2)	3428.3	21.88	
	Free OH(6)	3525.8	4.61	
0 mol H ₂ O	O(6)H...O(3')	3133.6	12.22	0.9994
	O(3)H...O(5)	3232.7	25.28	
	O(2)H...O(6)	3329.1	29.02	
	Free OH(2)	3424.3	22.61	
	Free OH(6)	3527.9	10.89	
1 mol H ₂ O	O(6)H...O(3')	3131.6	12.8	0.9995
	O(3)H...O(5)	3234.3	25.82	
	O(2)H...O(6)	3334.4	28.75	
	Free OH(2)	3431.1	21.97	
	Free OH(6)	3536.9	10.66	
2 mol H ₂ O	O(6)H...O(3')	3127.2	12.48	0.9992
	O(3)H...O(5)	3229.2	22.88	
	O(2)H...O(6)	3328.1	32.39	
	Free OH(2)	3428.6	21.33	
	Free OH(6)	3540.9	10.91	
3 mol H ₂ O	O(6)H...O(3')	3139.4	12.04	0.9993
	O(3)H...O(5)	3244.6	23.9	
	O(2)H...O(6)	3340.7	34.02	
	Free OH(2)	3441.9	20.39	
	Free OH(6)	3547.4	9.66	
4 mol H ₂ O	O(6)H...O(3')	3126.2	11.28	0.9993
	O(3)H...O(5)	3230.2	23.5	
	O(2)H...O(6)	3328.4	32.93	
	Free OH(2)	3430.1	22.59	
	Free OH(6)	3538.1	9.7	
5 mol H ₂ O	O(6)H...O(3')	3133.3	12.41	0.9988
	O(3)H...O(5)	3239.4	24.83	
	O(2)H...O(6)	3339.2	31.09	
	Free OH(2)	3441.3	21.89	
	Free OH(6)	3549.7	9.77	
6 mol H ₂ O	O(6)H...O(3')	3129.2	12.35	0.9993
	O(3)H...O(5)	3232.6	24.55	
	O(2)H...O(6)	3332.6	30.74	
	Free OH(2)	3430.8	21.23	
	Free OH(6)	3527.6	11.13	

7 mol H ₂ O	O(6)H...O(3')	3130.6	11.94	0.9992
	O(3)H...O(5)	3235.2	23.98	
	O(2)H...O(6)	3331.6	33.68	
	Free OH(2)	3435.8	21.65	
	Free OH(6)	3550.6	8.75	

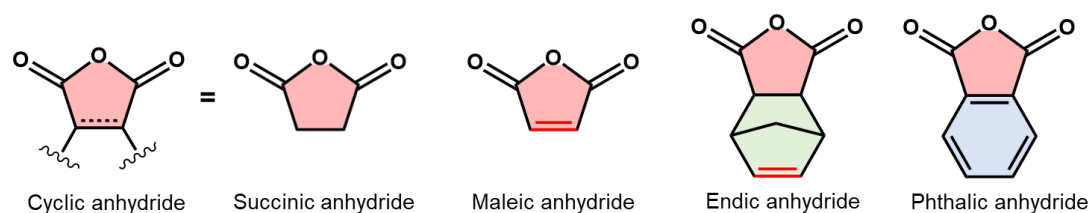
216

217 **Supplementary Table S3.** Relative content of hydrogen bonds and free hydroxyl
 218 groups in CNFs swollen with DES with different water contents (%).

Simple	Inter-chain H-bond	Intra-chain H-bonds	Free OH groups
HBKP	9.99	63.52	26.49
0 mol H ₂ O	12.22	54.57	33.5
1 mol H ₂ O	12.8	54.57	32.63
2 mol H ₂ O	12.48	55.27	32.24
3 mol H ₂ O	12.04	57.92	30.05
4 mol H ₂ O	11.28	56.42	32.29
5 mol H ₂ O	12.41	55.92	31.66
6 mol H ₂ O	12.35	55.29	33.17
7 mol H ₂ O	11.94	57.66	30.4

219

Supplementary Table S4. Parameters for preparing scalable functionalized CNFs using modified DES with different types of cyclic anhydrides.



Cyclic anhydride	DES: Cyclic anhydride (Weight ratio)	COOH (mmol/g)
SAH	1:1	2.024
MAH	1:1	1.412
EAH	1:1	1.075
PAH	1:1	0.501

Note: The modification time and temperature are both 2 h and 100 °C. Liquid separation and washing processes are both used 500 mesh nylon net.

225 **Supplementary Table S5.** Atomic concentrations from XPS spectra of scalable
 226 functionalized CNFs and their corresponding surface degree of substitution.

Sample	Carbon groups concentration (at%)				
	C-C	C-O	O-C-O	O-C=O	Surface DS
MAH-CNF(Melting)	23.05	53.75	19.92	3.28	0.152
MAH-CNF	23.11	55.19	17.96	3.74	0.169
SAH-CNF	39.22	46.3	8.84	5.62	0.303
PAH-CNF	39.11	50.34	7.43	3.11	0.155
EAH-CMF	49.38	37.91	9.39	3.31	0.218

227

228 **Supplementary Table S6.** Recovery, yield, carboxyl content, and degree of
 229 polymerization of CNFs prepared in 10 cycles of DES, compared with CNFs without
 230 DES swelling.

Cycle	Recovery (%)	Yield (%)	COOH (mmol/g)	DP
1	93.74	94.91	1.27	686
2	92.41	95.25	1.16	697
3	93.41	93.45	1.21	694
4	92.24	94.9	1.12	705
5	93.62	94.16	1.04	710
6	91.52	95.5	1.08	709
7	90.86	94.18	0.98	717
8	90.18	95.35	0.87	730
9	93.49	94.86	0.678	749
10	91.93	95.52	0.675	745
No swelling	-	96.62	0.573	743

231

Supplementary Table S7. Price estimation of materials required for CNF production using the DES-based highly efficient swelling-modification strategy, based on procurement prices from websites for 1 ton of pretreated pulp board.

Chemical	Purchase link	Price (CNY/t)	Dosage (t)	Cost (CNY/t)
Kraft pulp	https://detail.1688.com/offer/42385363860.html?spm=a261b.2187593.0.0.7c676138VuwH8J	4000	1.075	4300
Choline Chloride	https://detail.1688.com/offer/747781227383.html?spm=a261b.2187593.0.0.38003dacC6iF3K	4800	2.56	12288
Zinc Acetate	https://detail.1688.com/offer/965796273393.html?spm=a261b.2187593.0.0.6d3d764fvZJ2CP	2070	2	4140
Maleic Anhydride	https://detail.1688.com/offer/872783199856.html?spm=a261y.7663282.3002526303362591.2.34dc6b32tR8dAy&sk=order	6000	2.28	13680
All-in cost	34408 ¥			

Supplementary Table S8. Price estimation of raw materials for TOCN production *via* TEMPO oxidation, based on procurement prices from websites for 1 ton of pretreated pulp board.

Chemical	Purchase link	Price (CNY/t)	Dosage (t)	Cost (CNY/t)
Kraft Pulp	https://detail.1688.com/offer/42385363860.html?spm=a261b.2187593.0.0.7c676138VuwH8J	4000	1.075	4300
TEMPO	https://detail.1688.com/offer/775731008585.html?spm=a26352.13672862.offerlist.32.56b81e627N3iMD	850000	0.03	25500
Sodium Bromide	https://detail.1688.com/offer/938635337660.html?spm=a26352.13672862.offerlist.4.14951e62gg2HOc	24200	0.125	3025
Sodium Hypochlorite	https://detail.1688.com/offer/717135258542.html?spm=a26352.13672862.offerlist.1.f34b7f3c2ggWlu	5400	2.8	15120
Sodium Hydroxide	https://detail.1688.com/offer/895190908282.html?spm=a26352.13672862.offerlist.89.3f6d1e62z4yAZK	6600	1.5	9900
All-in cost	58454 ¥			

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