Supporting Information

Dissolution and Metastable Solution of Cellulose in NaOH/Thiourea at 8 °C for Construction of Nanofibers

Zhiwei Jiang,[†] Yan Fang,[†] Yanping Ma,[‖] Maili Liu,[‡] Ruigang Liu,[‖] Hongxia Guo,[‖] Ang Lu,[*,†] Lina Zhang [*,†]

[†]College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

[‡] State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan, 430071,

[‖]State Key Laboratory of Polymer Physics and Chemistry, Beijing National Laboratory of Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

*Corresponding authors. E-mail: zhangln@whu.edu.cn (L. Zhang), anglu@whu.edu.cn (A. Lu). Tel. & Fax: +86-27-87219274

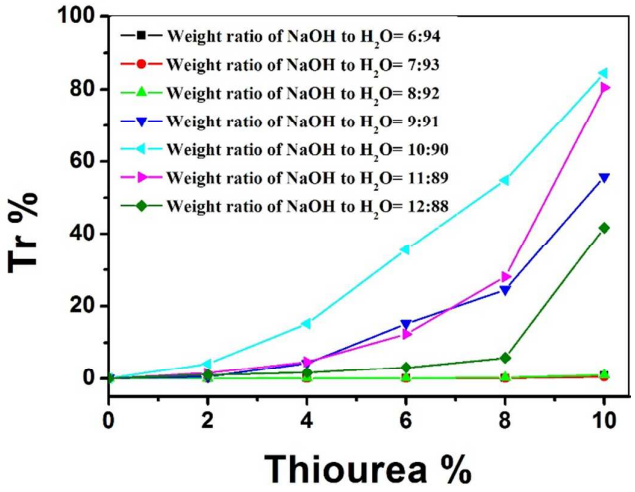

Figure S1. The transmittance of 1 wt% C-1 solution dissolved at 25 °C with different component ratio in NaOH/thiourea aqueous solution.

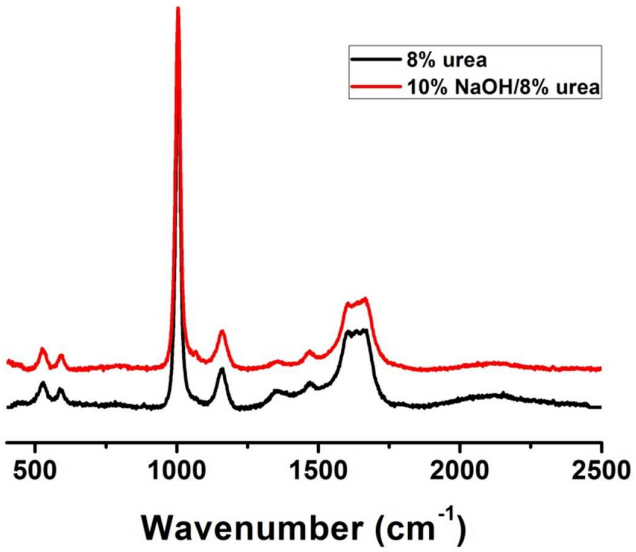

Figure S2. Raman spectra of 10 wt% NaOH/ 8 wt% urea and 8 wt% urea aqueous solutions

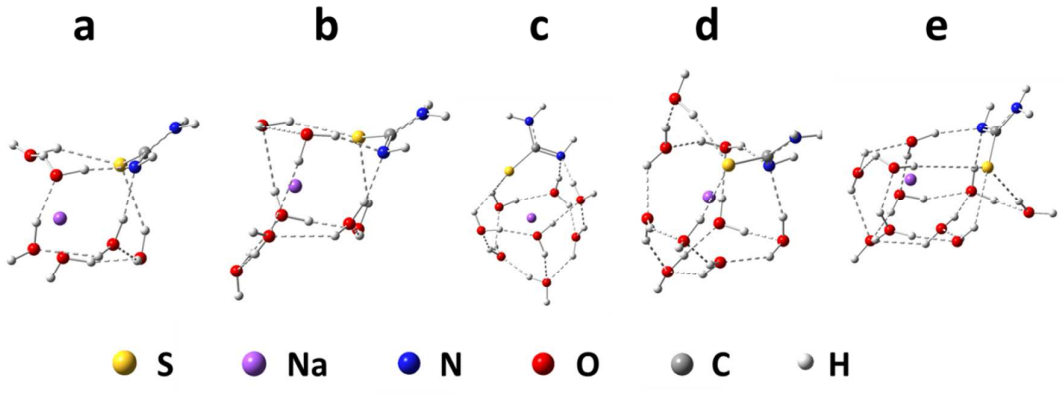

Figure S3. The optimized structures of (a) $NaOH(H_2O)_5$·thiourea, (b) $NaOH(H_2O)_6$·thiourea, (c) $NaOH(H_2O)_7$·thiourea, (d) $NaOH(H_2O)_8$·thiourea, and (e) $NaOH(H_2O)_9$·thiourea clusters by M06-2X/6-31++G(d,p) theoretical method.

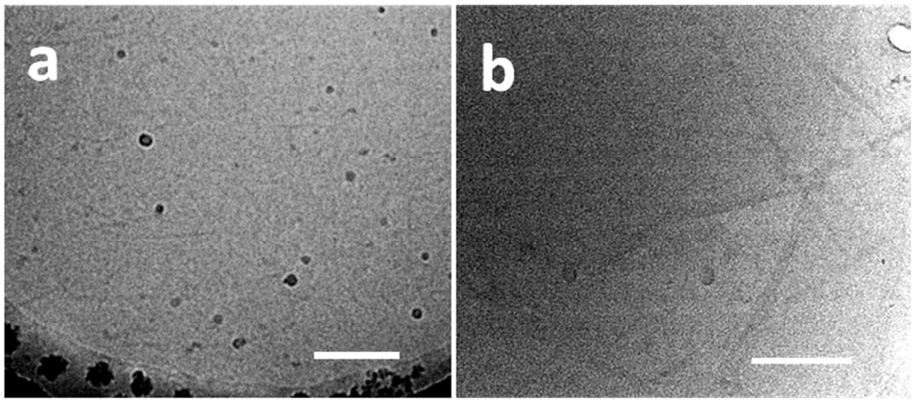

Figure S4. Cryo-TEM images of the cellulose dilute solution, a) the cellulose chains, b) the cellulose aggregates (scale bar=200 nm).

Table S1. ^{13}C NMR chemical shifts of cellulose in several solvent systems.

solvent system	^{13}C NMR chemical shift (ppm)					
	C1	C2	C3,5	C4	C6	Source
10 wt% NaOH	103.74	73.86	75.44	78.91	60.41	This work
Solvent-1	103.64	73.78	75.18	78.84	60.38	This work
Solvent-2	103.62	73.73	75.31	78.8	60.42	This work
NaOH/urea/D_2O	103.8	73.8	75.4	79.1	60.6	S1

Table S2. ^{15}N NMR chemical shifts of cellulose solution in several solvent systems.

Sample	^{15}N NMR chemical shift (ppm)
5 wt% thiourea	105.79
8 wt% thiourea	105.85
Solvent-1	119.48
Solvent-2	118.68
Solution-1	119.29
Solution-2	118.45

Table S3. Total binding energies (ΔE_n^{ZPE})[a] and successive binding energies ($\Delta E_{n,n\text{-}1}$)[b] $NaOH(H_2O)_n$·thiourea (n=5-9) clusters by M06-2X/6-31++G(d,p) theoretical method.

n	$NaOH(H_2O)_n$·urea	
	ΔE_n^{ZPE}/(kJ·mol^{-1})	$\Delta E_{n,n\text{-}1}$/(kJ·mol^{-1})
5	–266.6	-----
6	–275.4	–8.8
7	–287.3	–11.9
8	–295.7	–6.6
9	–303.6	–7.9

[a] $-\Delta E_n^{ZPE}=E^{ZPE}[NaOH(H_2O)_n\cdot thiourea]-E^{ZPE}[Na^+]-E^{ZPE}[OH^-]-E^{ZPE}[thiourea]-nE^{ZPE}[H_2O]$;

[b] $\Delta E_{n,n\text{-}1}=\Delta E_n^{ZPE}-\Delta E_{n\text{-}1}^{ZPE}$

Table S4. The Cartesian coordinates of the optimized geometry of $NaOH(H_2O)_5$·thiourea cluster in Figure S3 (a).

Center Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	O	-2.77939	-1.43411	-1.11723
2	H	-2.09699	-2.08853	-0.87522
3	Na	-1.39873	-0.06032	0.356903
4	O	-0.4978	-2.36064	-0.1257
5	H	-0.37947	-2.49722	0.821484
6	C	2.287364	-0.26206	-0.23798
7	N	3.642609	-0.10762	-0.19717
8	H	4.018763	0.604102	0.406254
9	H	4.214242	-0.43967	-0.95788
10	N	1.704179	-1.04526	-1.10742
11	H	0.354927	-1.99894	-0.48065

12	H	2.379917	-1.499	-1.72016
13	O	-0.25662	2.919607	-0.81848
14	H	-0.38672	2.198649	-1.45514
15	H	0.500906	2.607521	-0.30107
16	O	-2.2153	1.996892	0.783696
17	H	-3.00796	2.514897	0.92358
18	H	-1.59369	2.542728	0.25335
19	O	-0.64069	0.32453	-1.84161
20	H	0.192085	-0.19438	-1.7621
21	H	-1.29136	-0.22609	-2.28987
22	O	-0.69447	-1.18607	2.417379
23	H	-0.88111	-1.12862	3.35678
24	H	0.145068	-0.7084	2.263308
25	H	-3.60944	-1.90065	-1.22439
26	S	1.396835	0.652371	0.955709

Table S5. The Cartesian coordinates of the optimized geometry of $NaOH(H_2O)_6$·thiourea cluster in Figure S3 (b).

Center	Atomic	Coordinates (Angstroms)		
Number	Symbol	X	Y	Z
1	O	-2.52387	1.75183	0.433081
2	H	-2.77666	2.611759	0.09216
3	Na	-0.83244	0.477869	-0.51036
4	O	0.394366	2.369411	-0.84778
5	H	0.751635	2.724968	-1.66316
6	C	2.796836	0.10406	0.235205
7	N	4.113844	-0.24831	0.339333
8	H	4.36339	-1.19314	0.098798
9	H	4.71647	0.250402	0.975264
10	N	2.348293	1.240033	0.702816
11	H	1.175336	2.059605	-0.31906
12	H	3.089323	1.785823	1.13994
13	O	-0.36491	-2.12444	1.713111
14	H	-0.37154	-1.20819	2.036399
15	H	0.477133	-2.16379	1.234435
16	O	-2.0512	-1.53029	-0.2964
17	H	-1.72782	-1.85444	-1.14501
18	H	-1.49391	-1.92994	0.413573
19	O	-0.20141	0.673582	1.756496
20	H	0.709386	0.984436	1.556721
21	H	-0.77302	1.441881	1.859832
22	O	-0.54952	-0.63	-2.61653

23	H	-0.59603	-0.49344	-3.56485
24	H	0.392973	-0.7071	-2.3824
25	H	-3.3368	1.215647	0.50912
26	O	-4.3695	-0.23658	0.359058
27	H	-3.66933	-0.86779	0.107004
28	H	-4.90884	-0.67253	1.020884
29	S	1.777972	-1.0622	-0.5669

Table S6. The Cartesian coordinates of the optimized geometry of $NaOH(H_2O)_7$·thiourea cluster in Figure S3 (c).

Center	Atomic	Coordinates (Angstroms)		
Number	Symbol	X	Y	Z
1	O	-1.46715	2.170008	0.722639
2	H	-0.98272	2.553742	-0.02609
3	Na	-0.63095	-0.03816	0.429761
4	O	0.407391	2.326876	-1.31506
5	H	0.775208	2.948123	-1.94789
6	C	2.80516	0.010983	-0.24399
7	N	4.110694	-0.36761	-0.32556
8	H	4.320891	-1.3438	-0.44408
9	H	4.850977	0.258524	-0.0528
10	N	2.465528	1.251412	0.036804
11	H	1.198068	1.92156	-0.82842
12	H	3.286013	1.840121	0.175757
13	O	-0.21064	-1.65531	2.269928
14	H	0.163576	-0.84145	2.643306
15	H	0.514747	-2.0146	1.740524
16	O	-2.5775	-1.43597	0.673419
17	H	-2.25066	-2.00638	-0.05142
18	H	-2.14672	-1.75733	1.477893
19	O	0.651293	1.013443	2.216069
20	H	1.36437	1.200175	1.568239
21	H	0.044143	1.7618	2.173623
22	O	-1.31995	-2.45108	-1.53728
23	H	-1.21029	-1.55899	-1.90769
24	H	-0.43917	-2.83656	-1.54131
25	H	-2.39088	2.071263	0.451368
26	O	-3.75794	0.852597	-0.25607
27	H	-3.53155	-0.00163	0.162796
28	H	-4.7153	0.902934	-0.29219
29	O	-1.44258	0.300073	-1.79006
30	H	-0.79825	1.015989	-1.9268

31	H	-2.3158	0.696526	-1.66596
32	S	1.62974	-1.22549	-0.55123

Table S7. The Cartesian coordinates of the optimized geometry of $NaOH(H_2O)_8$·thiourea cluster in Figure S3 (d).

Center	Atomic	Coordinates (Angstroms)		
Number	Symbol	X	Y	Z
1	O	-1.60515	-2.14103	0.292656
2	H	-1.36828	-2.48743	-0.57935
3	Na	-0.44414	-0.027	0.256718
4	O	2.724888	-2.01699	1.827192
5	H	3.558522	-1.7589	2.224972
6	C	2.200473	0.993851	-0.66754
7	N	3.390471	1.525545	-1.07024
8	H	3.970002	0.980364	-1.68583
9	H	3.539085	2.522078	-1.03534
10	N	1.305527	1.688692	-0.016
11	H	2.722448	-1.64995	0.924201
12	H	1.637224	2.644272	0.129567
13	O	-1.21663	2.778879	-1.14096
14	H	-1.5171	2.07383	-1.73185
15	H	-0.31102	2.507305	-0.92288
16	O	-2.21245	1.43088	1.05027
17	H	-1.65186	1.643121	1.820298
18	H	-2.01486	2.105277	0.369559
19	O	-0.52829	-2.18466	-2.39669
20	H	0.291748	-1.71324	-2.15257
21	H	-0.29772	-2.78063	-3.11341
22	O	-0.02518	1.541548	2.707392
23	H	0.028792	0.602548	2.941203
24	H	0.611576	1.63144	1.981997
25	H	-2.53314	-1.86446	0.24574
26	O	-3.86044	-0.47006	0.161937
27	H	-3.43839	0.260778	0.663642
28	H	-4.8024	-0.44073	0.339873
29	O	0.144708	-1.20242	2.277273
30	H	1.052955	-1.5582	2.274309
31	H	-0.43129	-1.90793	1.955547
32	O	-1.88438	0.144379	-1.74516
33	H	-2.74915	-0.08325	-1.37065
34	H	-1.60921	-0.61514	-2.2793
35	S	1.989138	-0.70758	-1.03038

Table S8. The Cartesian coordinates of the optimized geometry of $NaOH(H_2O)_9$·thiourea cluster in Figure S3 (e).

Center Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	O	1.60755	2.924339	-0.60776
2	H	0.846843	3.056369	-0.02239
3	Na	0.901273	-0.57132	-0.47311
4	O	-0.9476	2.461135	0.611257
5	H	-1.56625	2.484657	1.357887
6	C	-2.78099	-0.21792	-0.84524
7	N	-3.92857	-0.84128	-1.24996
8	H	-4.21974	-1.66494	-0.75132
9	H	-4.627	-0.32635	-1.76327
10	N	-2.42444	0.953755	-1.28171
11	H	-1.45507	1.991873	-0.09303
12	H	-3.1176	1.34663	-1.91773
13	O	0.576461	-2.81426	-1.0388
14	H	0.597768	-3.19204	-1.92112
15	H	-0.36179	-2.72524	-0.80154
16	O	2.777583	-1.6219	0.731989
17	H	2.125256	-1.98639	1.362874
18	H	2.821383	-2.22911	-0.01346
19	O	0.291929	0.961742	-2.08885
20	H	-0.67581	1.020877	-1.95572
21	H	0.667998	1.791664	-1.74604
22	O	0.649237	-1.95516	2.39292
23	H	0.455714	-1.00623	2.299861
24	H	-0.18212	-2.41234	2.24145
25	H	2.256666	2.407973	-0.1118
26	O	3.546509	0.99807	0.594081
27	H	3.38966	0.036689	0.710237
28	H	4.427489	1.180799	0.929144
29	O	0.866327	0.644734	1.499988
30	H	0.172473	1.30734	1.286471
31	H	1.677346	1.120911	1.707507
32	O	2.774798	-0.28913	-1.92992
33	H	3.294302	0.404461	-1.5065
34	H	2.163817	0.167917	-2.52261
35	O	-2.50318	1.237164	2.504995
36	H	-2.33592	0.436036	1.977086
37	H	-3.3157	1.075016	2.987324

38	S	-1.8071	-1.11598	0.306555

Reference

(S1) Cai, J.; Zhang, L., Rapid Dissolution of Cellulose in LiOH/Urea and NaOH/Urea Aqueous Solutions. *Macromol. Biosci.* **2005,** *5* (6), 539-548, doi: 10.1002/mabi.200400222