Formic acid-hydrogen peroxide treatment of furfural residue for production of nanocellulose, lignin, and nano-scale lignin

Minmin Chang[a,+], Xiaohui Wang[a,b,+], Qixuan Lin[a], Rui Li[a], Lihong Zhao[a], Junli Ren[a,*] Fengshan Zhang[c]

[a] State Key Laboratory of Pulp and Paper Engineering, School of Light Industry and Engineering, South China University of Technology, Guangzhou 510640, China.

[b] State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Jinan 250353, China.

[c] Shandong Huatai Paper Company limited, Dongying 257335, China.

[+] These authors contributed equally to this work.

Corresponding Author:

Junli Ren: renjunli@scut.edu.cn; Telephone: ＋8620-8711186

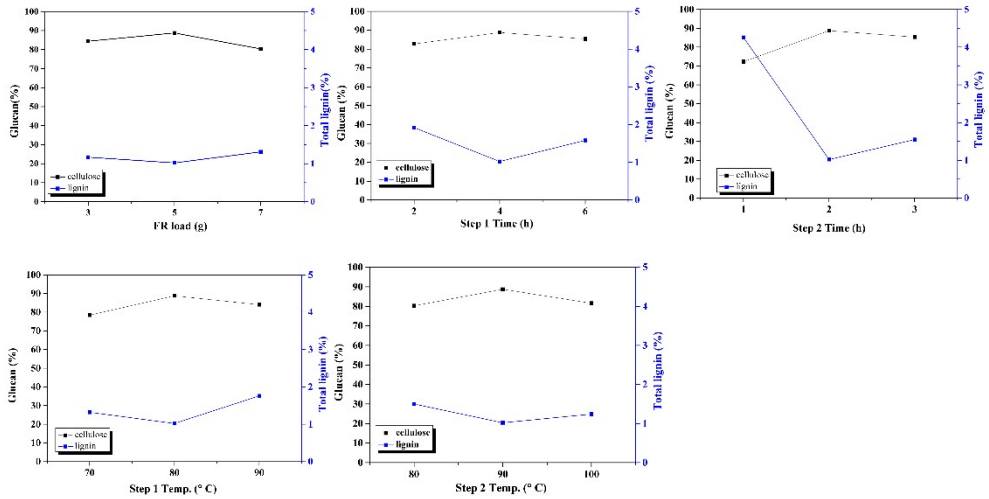


Figure S1. Cellulose content and residual lignin of solid residue under different conditions (Temp., Time and FR load).

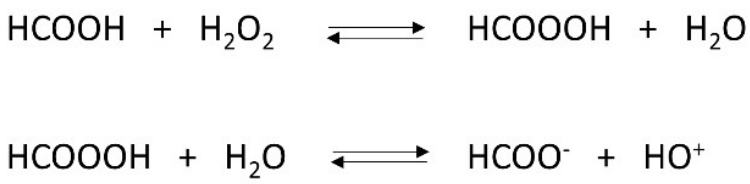


Figure S2. The reaction between formic acid and hydrogen peroxide.

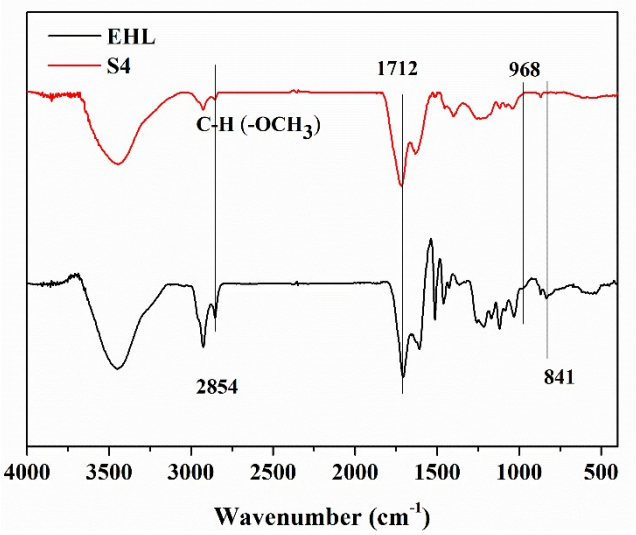


Figure S3. FTIR spectra of EHL extracted from furfural residue and recovery lignin (S4).

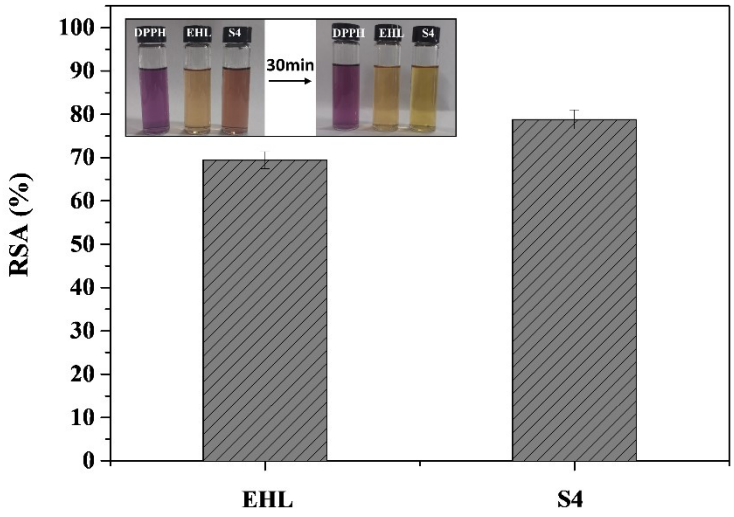


Figure S4. DPPH radical scavenging ability (RSA) of EHL and S4 lignin.

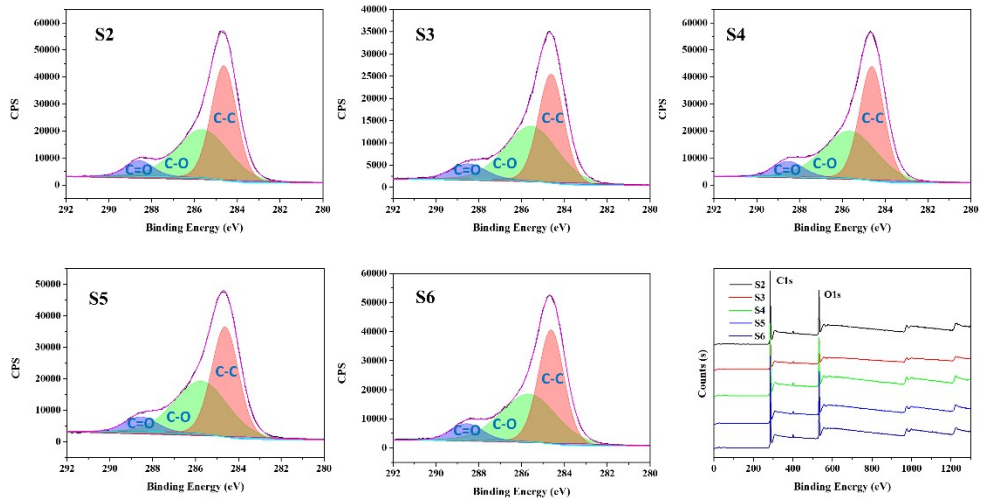


Figure S5. High-resolution C 1s spectra of nanoscale lignin (S2~S6).

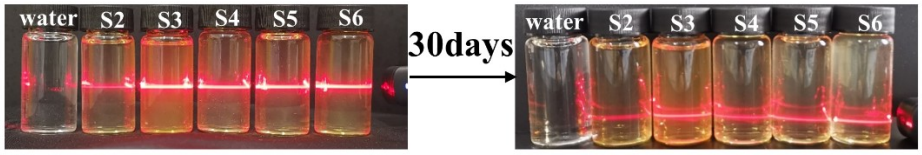


Figure S6. Stability of nano-scale lignin dispersion.

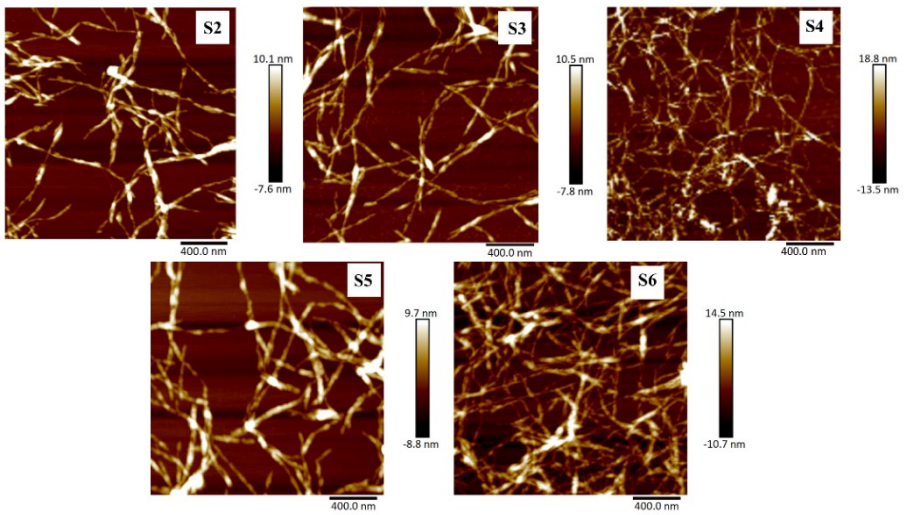


Figure S7. AFM images of nanocellulose with a concentration of 0.5 wt% (S2~S6).

Table S1. Component analysis of solid residue after treatment by different conditions.

Samples	Glucan	Insoluble lignin	Soluble lignin	Ash	Total
1	29.6%	63.0%	1.12%	1.2%	94.92%
2	79.41%	1.32%	0.44%	5.36%	86.53%
3	88.73%	0.80%	0.50%	6.93%	97.17%
4	84.00%	1.76%	0.44%	6.05%	92.26%
5	81.30%	1.50%	0.47%	4.52%	87.80%
6	82.61%	1.24%	0.52%	3.75%	88.12%
7	82.71%	1.92%	0.40%	7.25%	92.29%
8	85.36%	1.58%	0.44%	6.28%	93.66%
9	81.29%	4.26%	0.47%	3.69%	88.71%
10	80.34%	1.55%	0.49%	4.43%	86.80%
11	85.38%	1.17%	0.44%	7.07%	94.06%
12	81.34%	1.31%	0.57%	5.15%	88.37%

Table S2. Treatment conditions for different reactions.

Samples	FR-FA-H_20_2 (g-mL-mL)	Step1 Temp. (℃)	Step2 Temp. (℃)	Step1 time (h)	Step2 time (h)
1	-	-	-	-	-
2	5–40–16	70	90	4	2
3	5–40–16	80	90	4	2
4	5–40–16	90	90	4	2
5	5–40–16	80	80	4	2
6	5–40–16	80	100	4	2
7	5–40–16	80	90	2	2
8	5–40–16	80	90	6	2
9	5–40–16	80	90	4	1
10	5–40–16	80	90	4	3
11	3–40–16	80	90	4	2
12	7–40–16	80	90	4	2

Table S3. Yields of precipitated lignin and nano-scale lignin (Based on theoretical lignin value of FR).

Samples	Lignin yields (%)	Nano-scale lignin yields (%)	Total yields (%)
S2	37.14	6.55	43.69
S3	30.74	15.90	46.63
S4	28.04	11.89	39.93
S5	30.95	10.61	41.56
S6	24.59	9.33	33.82

Table S4. Assignment of $^{13}C/^{1}H$ correlation of signals in the 2D-NMR.

Label	δ_C/δ_H	Assignment
<u>Lignin signals</u>		
$-OCH_3$	55.6/3.73	C/H in methoxyls
A_γ	59.4/3.72	C_γ/H_γ in normal (γ-hydroxylated) β-*O*-4′ substructures (A)
A'_γ	62.7/3.83-4.30	C_γ/H_γ in γ-acylated β-*O*-4′ substructures (A′)
Iγ	60.54/4.53	Cγ-Hγ in spirdienone substructures (D)
$A_{\beta(S)}$	85.9/4.12	C_β/H_β in β-*O*-4′ substructures linked to a S unit (A)
$S_{2,6}$	103.8/6.69	C_2/H_2 and C_6/H_6 in etherified syringyl unites (S)
$S'_{2,6}$	106.4/7.19	C_2/H_2 and C_6/H_6 in α-oxidized syringyl unites (S′)
PCA_β/FA_β	113.5/6.27	C_β/H_β in *p*-coumarates (PCA) and ferulates (FA)
$H_{3,5}$	114.5/6.62	C_3/H_3 and C_5/H_5 in *p*-hydroxyphenyl units (H)
G_6	118.7/6.77	C_6/H_6 in guaiacyl units (G)
$PCA_{3,5}$	115.5/6.77	C_3/H_3 and C_5/H_5 in *p*-coumarates (PCA)
$H_{2,6}$	128.0/7.20	C_2/H_2 and C_6/H_6 in *p*-hydroxyphenyl units (H)
$PCA_{2,6}$	130.8/7.46	C_2/H_2 and C_6/H_6 in *p*-coumarates (PCA)

$P_{2,6}$	131.5/7.91	C_2/H_2 and C_6/H_6 in *p*-hydroxybenoate (P)
PCA_α/FA_α	144.4/7.45	C_α/H_α in *p*-counmarates (PCA) and ferulates (FA)
Carbohydrate signals		
$Gl_{6(I+R)}$	60.6/3.60 and 3.80	C_6/H_6 in (1→4)-β-D-glucopyranoside (I+R)
$Gl_{6(NR)}$	62.7/3.35 and 3.47	C_6/H_6 in β-D-glucopyranoside (NR)
$Gl_{4(NR)}$	70.1/3.02	C_4/H_4 in β-D-glucopyranoside (NR)
$Gl_{2(I)}$	73.2/3.05	C_2/H_2 in (1→4)-β-D-glucopyranoside (I)
$Gl_{3(I)}$	74.6/3.35	C_3/H_3 in (1→4)-β-D-glucopyranoside (I)
$Gl_{5(I)}$	76.4/3.15	C_5/H_5 in (1→4)-β-D-glucopyranoside (I)
$Gl_{4(I)}$	80.5/3.32	C_4/H_4 in (1→4)-β-D-glucopyranoside (I)
$\alpha Gl_{1(R)}$	92.1/4.92	C_1/H_1 in α-D-glucopyranoside (R)
$\beta Gl_{1(R)}$	96.5/4.25	C_1/H_1 in β-D-glucopyranoside (R)
$Gl_{1(I+NR)}$	102.6/4.31	C_1/H_1 in (1→4)-β-D-glucopyranoside (I+NR)

Table S5. Pyrolysis products determined by PY-GC-MS from fast pyrolysis of EHL at 500 ℃.

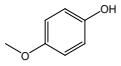
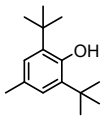
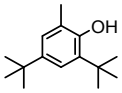
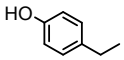
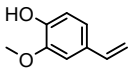
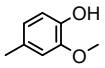
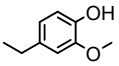
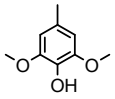
Type	Relative amount (%)	Compounds	Structure
H	69.72%	Mequinol	
		Butylated hydroxytoluene	
		Phenol, 4,6-di(1,1-dimethylethyl)-2-methyl-	
		Phenol, 4-ethyl-	
G	27.73%	Creosol	
		Phenol, 4-ethyl-2-methoxy-	
		2-Methoxy-4-vinylphenol	
S	2.53%	3,5-Dimethoxy-4-hydroxytoluene	

Table S6. Pyrolysis products determined by PY-GC-MS from fast pyrolysis of recovery lignin (S4) at 500 ℃.

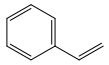
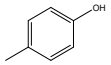
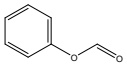
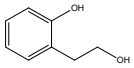
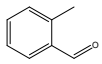
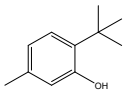
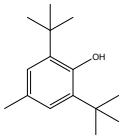
Compounds	Structure
Styrene	
Phenol	
p-Cresol	
Formic acid phenyl ester	
Benzeneethanol, 2-hydroxy-	
Benzaldehyde, 2-methyl-	
Phenol, 2-(1,1-dimethylethyl)-5-methyl-	
Butylated Hydroxytoluene	

Table S7. Purity of recovered lignin (S4) determined by NREL method.

	Insoluble lignin	Soluble lignin	Cellulose	Purity
S4	87.9%	1.8%	0.7%	89.7%

Table S8. The content of the C 1s peaks and O/C ratio.

	C-C (%)	C-O (%)	C=O (%)	O/C (%)
S2	284.60 (49.94%)	285.61 (43.01%)	288.56 (7.04%)	0.273
S3	284.60 (48.71%)	285.52 (43.50%)	288.50 (7.79%)	0.277
S4	284.60 (45.31%)	285.62(46.29%)	288.52(8.20%)	0.291
S5	284.60 (47.71%)	285.71 (44.74%)	288.54 (7.54%)	0.286
S6	284.60 (48.49%)	285.63 (43.22%)	288.55 (8.30%)	0.298

Table S9. Yields of nanocellulose (based on theoretical value of cellulose in FR).

Samples	Yields (%)
S2	52.3
S3	27
S4	27.1
S5	27.3
S6	26.4