Supplementary Information

Enabled Cellulose Nanopaper with Outstanding Water Stability and Wet Strength via Activated Residual Lignin as a Reinforcement

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Supplementary Note S1. Circulating reaction system for nitric acid solutions.

The bamboo powder was pretreated with HNO_3 and H_2O_2 for 24 h, and other experimental conditions were consistent with the description in the Experimental Section. After treatment, the mixture was filtered to produce a cellulose-rich solid and a filtrate containing HNO_3. The concentrations of HNO_3 and H_2O_2 in the filtrate were tested. The concentration of HNO_3 was determined by titration with 1.000 mol/L NaOH standard solution, and the concentration of H_2O_2 was determined by titration with 0.100 mol/L potassium permanganate standard solution. The concentrations of HNO_3 and H_2O_2 present during cycles of the process are shown in Table S4. The initial concentrations of HNO_3 and H_2O_2 were 2.75 mol/L and 1.03 mol/L, respectively. After the first reaction, the concentrations of HNO_3 and H_2O_2 in the filtrate were 2.73 mol/L and 0.82 mol/L, respectively. During the treatment, only a small amount of HNO_3 was consumed, which is consistent with previous studies.[1] Each treatment consumed approximately 20% of the H_2O_2. In summary, to ensure normal operation of the cyclic reaction system, only approximately 0.01 mol/g H_2O_2 must be added after every cycle, and approximately 0.006 mol/g HNO_3 must be added after every five cycles.

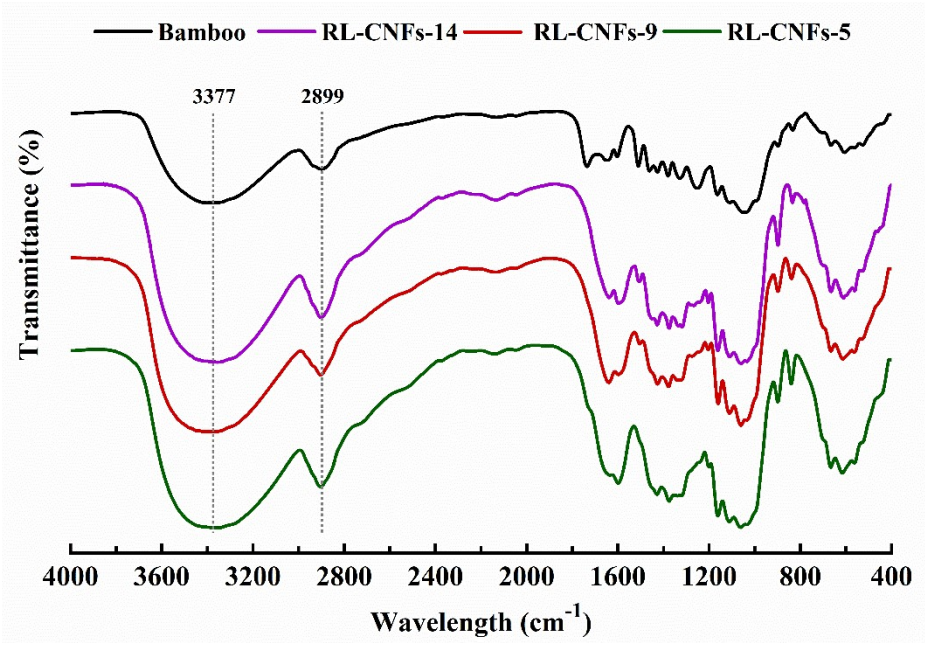

Fig. S1 FTIR spectra of bamboo and RL-CNFs (4000-400 cm^{-1}).

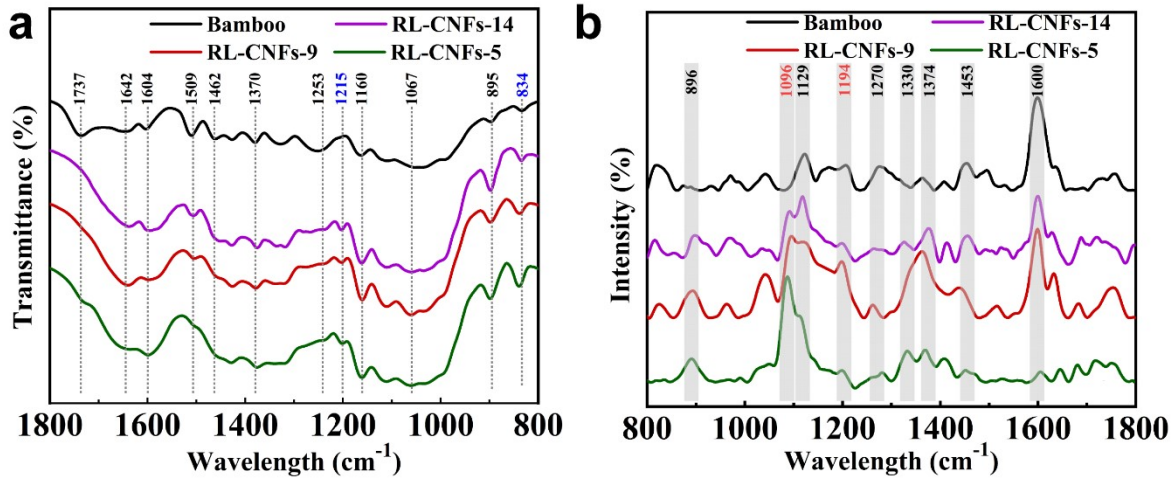

Figure. S2 (a) FTIR spectra of bamboo and RL-CNFs (1800-800 cm^{-1}); (b) Raman pattern of bamboo and RL-CNFs.

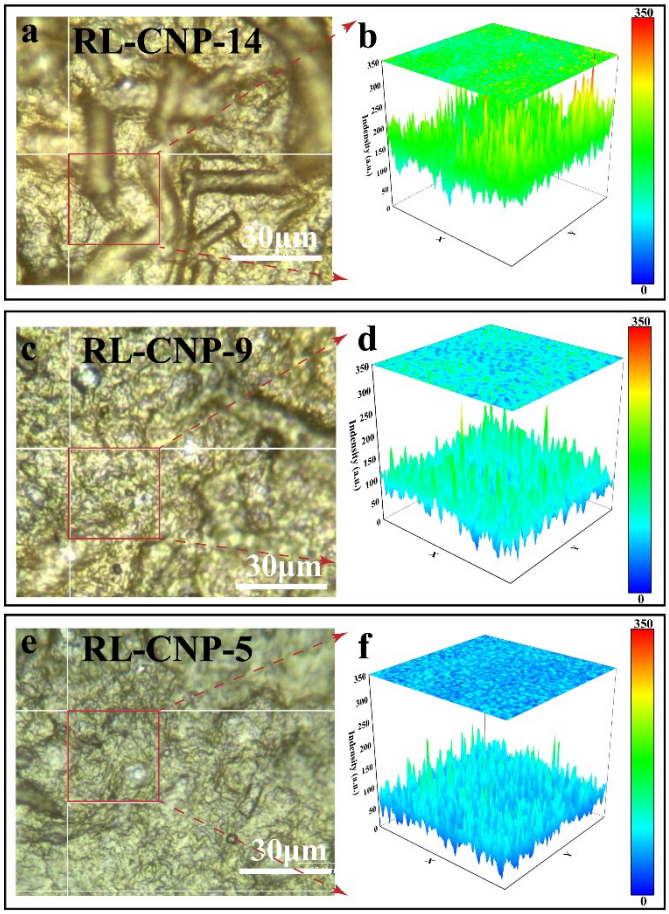

Fig. S3 Raman electron microscope image of ARL-CNP and the Raman mapping image of the location: (a) (b) RL-CNP-14, (c) (d) RL-CNP-9 and (e) (f) RL-CNP-5.

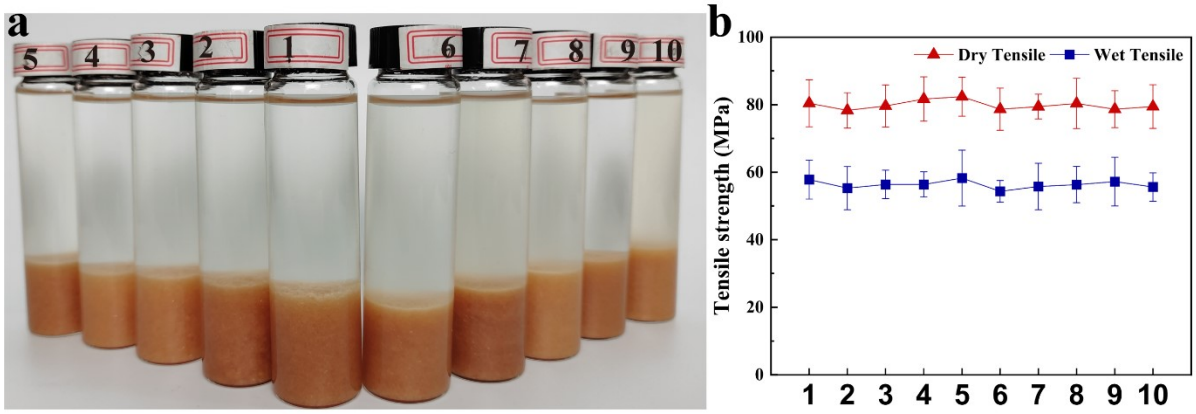

Fig. S4 Cellulose-rich fiber solution after 10 cycles of the nitric acid solution circulation reaction system (a); wet and dry tensile strengths of RL-CNP (b).

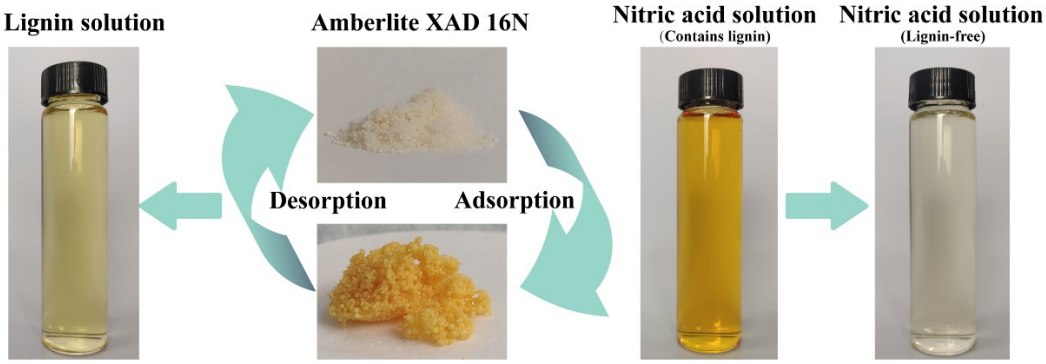

Fig. S5 Amberlite XAD16N adsorbs lignin in HNO_3.

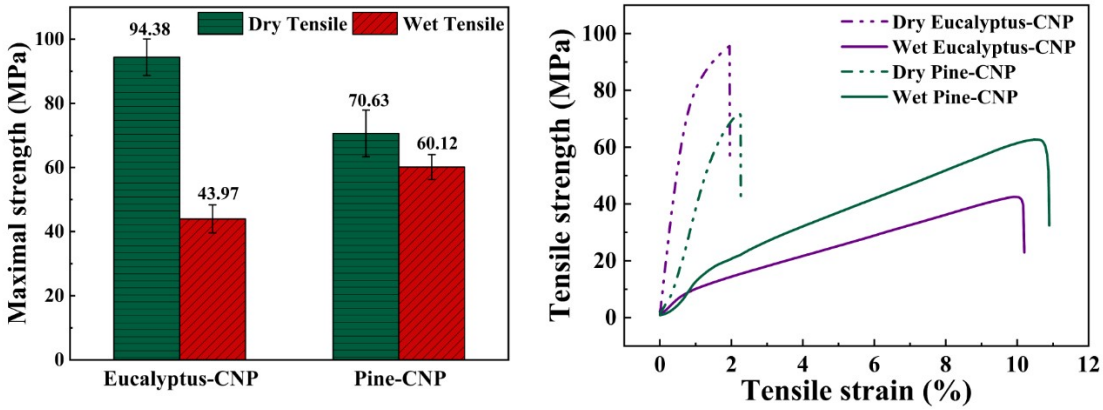

Fig. S6 Diagram of dry and wet tensile strengths for Eucalyptus-CNPs (with 11.18% lignin content) and Pine-CNPs (with 14.36% lignin content): (a) histograms; (b) graphs.

Table S1. Distribution of functional groups of bamboo and ARL-CNFs in FTIR spectrum.[2-4]

Wavenumber (cm^{-1})	Assignment	Attributed
3377	O−H stretching	Cellulose
2899	C−H stretching	Cellulose
1737	C-O carbonyl band, C=O stretching vibrations of the acetyl groups of galactoglucomannan, carboxyl- and aldehydes and aromatic/conjugated aldehydes and esters	Lignin and hemicellulose
1642	O-H bending vibrations	Cellulose
1604	Aromatic skeleton vibration	Lignin
1509	C=C stretching vibration in aromatic ring	Lignin
1462	Aromatic ring C-H deformation	Lignin
1370	C-H bending, $-CH_3$ (lignin), $-CH_2$ (carbohydrates), lignin-carbohydrate complexes bonds	Lignin and carbohydrate
1253	C-O Stretching vibration	Hemicellulose
1215	C-O of phenol [5]	Lignin
1160	C−O stretching	Cellulose
1067	C-O-C pyranose ring skeletal vibration	Cellulose
895	β-glycosidic bond	Cellulose
834	O-H of phenolic hydroxyl	Lignin

Table S2. Distribution of the functional groups of bamboo fiber and ARL-CNFs in the Raman spectrum [6].

Wavenumber (cm^{-1})	Assignment	Attributed
896	H-C-C and H-C-O bending at C6[7, 8]	Cellulose
1096	C-C-O stretch of phenol[7-10]	Lignin
1129	Coniferaldehyde/sinapaldehyde[7-10]	Lignin
1194	A phenol mode[7, 9]	Lignin
1270	Aryl-O-CH_3 and aryl-O of aryl-OH; guaiacyl/syringyl ring (with C=O group)[8, 9]	Lignin
1330	Aliphatic O-H bend[7-11]	Cellulose
1374	C-H bend in R_3C-H[9]	Cellulose
1453	CH_3 bending in OCH_3[7-10]	Lignin and carbohydrate
1600	Aryl ring stretch, symmetric[7-10]	Lignin

Table S3. Summary of published main results on wet tensile strength of CNF materials.

Ref.	Sample	Wet tensile strength (MPa)	Methods and Characteristics
This work	LF-CNP	4.12 ± 1.54	Retained with lignin-carbohydrate complex Solvent: water High yield (60.88%) based on biomass
	ARL-CNP with 5% lignin	41.46 ± 4.22	
	ARL-CNPwith 14% lignin	68.91 ± 3.50	
12	NFC	3.1±0.1	Carboxymethylated and cross-linked with glycidyltrimethylammonium chloride (GTMA) Post-treatment process
	NFC/CMC+(10%) GTMA	36±9	
	NFC/CMC+(15%) GTMA	42±13	
13	OCNF- aldehydes	~12	Oxidized by sodium periodate and then grafted with aldehydes Post-treatment process
14	CNF	1.2±0.1	Grafted with hydrophobic alkyl Post-treatment process esterificated with acetic, butyric, hexanoic and 2 dodecen-1-yl-succinnic anhydrides
	CNF-2 (acetic)	2.8±0.2	
	CNF-4 (butyric)	1.8±0.1	
	CNF-6 (hexanoic)	2.1±0.1	
	CNF-16 (2 dodecen-1-yl-succinnic anhydrides)	4.4±0.8	
15	Unmodified CNP	2.3±1.53	Cross-linked by citric acid and sodium hypophosphate Post-treatment process
	Crosslinked CNP	13.7±6.28	
16	TCNF-(10%) 88PVA	29.7 ± 4.7	TEMPO/$NaClO_2$-oxidized and bonded with poly (vinyl alcohol) (PVA) Post-treatment process
	TCNF-(25%)88PVA	21.5 ± 2.5	
	TCNF-(10%)98PVA	33.4 ± 6.0	
	TCNF-(25%)98PVA	22.9 ± 5.5	
17	CNF	11± 2	Grafted or bonded with aromatic mono-epoxy (phenylglycidylether, PGE) Post-treatment process
	CNF-bonded-PGE	9± 1	
	CNF-grafted-PGE	70±4	
18	CNF	18.0 ± 0.5	Residual free lignin particles were dispersed using organic solvents Solvent: dimethylacetamide (DMAC)
	CNF with 6% lignin	17.6±4.2	
	CNF with 10% lignin	19.8±1.3	
	CNF with 12% lignin	44.3 ± 2.3	
	CNF with 14% lignin	83.5 ± 12	
19	CNF-Alginate	~17	Entangled with the algal polysaccharides alginate Post-treatment process
20	CNF	2.8 ± 0.3	Dispersed with vitrimer nanoparticles Post-treatment process
	CNF_{65}/VP_{35}	31 ± 5	
	CNF_{50}/VP_{50}	22 ± 1	
21	CNF	0.9±0.1	Grafted with gelatin Post-treatment process
	CNF-gelatin	33.0 ± 2.3	
22	CNF with 5% lignin	<5	Retained lignin
	CNF with 21% lignin	<10	

Table S4. Concentrations and amounts used for supplementation of HNO_3 and H_2O_2 levels in the nitric acid solution circulation reaction system.

Times	HNO_3 concentration mol/L	H_2O_2 concentration mol/L	H_2O_2 supplementation mol/g	HNO_3 supplementation mol/g
0	2.75	1.03		
1	2.73	0.82	0.0097	
2	2.70	0.76	0.0125	
3	2.67	0.73	0.0138	
4	2.67	0.76	0.0125	
5	2.63	0.77	0.0120	0.0055
6	2.76	0.75	0.0129	
7	2.72	0.76	0.0125	
8	2.68	0.80	0.0106	
9	2.64	0.78	0.0115	
10	2.59	0.75	0.0129	

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