Supporting Information

Pre-phosphorylation for facile production of phosphorylated cellulose nanocrystals with high charge content: An optimized design and life cycle assessment

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Number of Tables: 6

Number of Figures: 4

Table S1 Comparison of production processes and properties of P-CNCs prepared from different manufacturing methods.

Modification types	Raw materials	Cellulose content (wt%)	Phosphorylation methods	Crystallinity index (%)	Size (L, D)	Charge content (mmol/kg)	Zeta potential (mV)	Yield (%)	Ref.
In-situ phosphorylation	Giant reed	33–49.4	Phosphoric acid hydrolysis (9 mol/L, 2 h, 60 °C)	83	L/D=33	254	NA	NA	1
	Tomato plant residue	33	Phosphoric acid hydrolysis (9 mol/L, 2 h, 100 °C)	81	L=670±115 nm D=6.2±2.4 nm	79.2	–37.3	NA	2
	Eggplant plant residue	62.5	Phosphoric acid hydrolysis (9 mol/L, 2 h, 100 °C)	73	L=597.5±163.1 nm D=6.3±2.3 nm	116.7	–39.4	NA	3
	Hardwood kraft pulp	NA	Phosphoric acid hydrolysis (75 wt%, 5 h, 70 °C)	82	L=200 nm D=8–15 nm	200	–31	NA	4
	Date palm sheath	42.7	Phosphoric acid hydrolysis (10.7 mol/L, 30 min, 90 °C)	83	L=94.77 nm D=16.42 nm	0.23[a]	–12.7	55.57	5
	Cellulose bioethanol residue	50	Phosphoric acid hydrolysis (10.7 mol/L, 30 min, 100 °C)	83	L=610 nm	435.21	–28[b]	85–89	6
	Cellulose bioethanol residue	50	Phosphoric acid in molten urea (10.7 mol/L, 30 min, 150 °C)	86	D=5–10 nm	1038.05	–35[b]	91	6
	Cotton/Filter paper	NA	Phosphoric acid hydrolysis (10.7 mol/L, 90 min, 100 °C)	81	L=316±127 nm D=31±14 nm	10.8±2.7	NA	76–80	7
Post-phosphorylation	CNCs	100	CNC:P_4O_{10}:urea =1:1:10, ball-milling mechanochemical process, 90 min	21	L=107±46 nm D=12±2 nm	3300	NA	NA	8
	CNCs	100	1 wt% CNC dispersion, $(NH_4)_2HPO_4$:urea=1:5, drying at 70 °C and curing at 150 °C for 60 min	50.2	NA	1478	–35	NA	9,10
Pre-phosphorylation	MCC	100	MCC:$NH_4H_2PO_4$:urea=1:0.3:1.2, drying at 70 °C and curing at 150 °C for 30 min	87.3	L=240±90 nm D=11.9±5.6 nm	2334	–27.1	92.4	This work

[a] The degree of substitution (DS) was calculated from conductometric titration, DS=(162×V_{eq}×C_{NaOH})/(m-y× V_{eq}×C_{NaOH}). [b] Measurement at pH=7.5. [c] NA: Not available.

Table S2 Input and output data of Route 1, 2, and 3 with the function unit of 1 g of P-CNCs.

Categories			**Unit**	**Value**			**Background data source**
				R1[a]	**R2**[b]	**R3**[c]	
Input	Materials	Paper pulp	g	1.202	1.282	2.164	Bleached softwood kraft pulp from the reference
		H_3PO_4 (v/v=85%)	g	/	217.814	/	Phosphate, market average (China); CLCD-China-ECER 0.8
		H_2SO_4 (98 wt%)	g	0.018	/	16.688	Sulfuric acid, market average (China); CLCD-China-ECER 0.8
		CaO	g	0.01		/	Lime production (China); lcacontest-s-85y6@ike-global.com 1.0
		NaOH (30 wt%)	g	/	/	44.461	Sodium hydroxide (30%), market average (China); CLCD-China-ECER 0.8
		NaClO (available chlorine 15%)	g	/	/	0.071	Sodium hypochlorite (available chlorine 15%) (China); CLCD-China-ECER 0.8
		$(NH_4)_2HPO_4$	g	/	/	0.883	Diammonium hydrogen phosphate (China); CLCD-China-ECER 0.8
		$NH_4H_2PO_4$	g	0.234	/	/	Ammonium dihydrogen phosphate (China); CLCD-China-ECER 0.8
		$CO(NH_2)_2$	g	0.487	/	2.007	Urea (China); CLCD-China-ECER 0.8
		Water	g	286.819	2993.590	3377.434	Tap water (China, industrial); CLCD-China-ECER 0.8
		Total	g	287.77	3212.686	3443.708	
	Heat	Natural gas	g	0.12	/	/	Natural gas (China); CLCD-China-ECER 0.8
		Heat	kJ	5.411	/	/	Heat (China, at a temperature level of

							55°C); ELCD 3.0
	Electricity	P-CNC production	kW·h	0.565	0.365	0.983	China power grid transmission (China, to users); display@ike-global.com 0.9
Output	Product	P-CNCs (1.0%)	g	100	100	100	
	Wastewater	Water	g	188.201	2937.305	3317.853	
		H_3PO_4	g	/	197.579	/	
		P	g	0.017	62.5	0.207	
		N	g	0.074	/	0.22	
		BOD	g	0.192	0.334	1.414	
		COD	g	0.205	0.334	3.02	
	Waste gas	NH_3	g	0.221	/	1.097	
	Waste	$CaSO_4$	g	0.025	/	/	
		Na_2SO_4	g	/	/	23.68	
		Sludge	g	0.119	/	/	

Assumptions:

1. MCC in Route 1 was produced from the paper pulp.

2. The total P in Route 2 was discharged into the wastewater in the form of H_3PO_4.

3. The yield of post-phosphorylation during P-CNC production in Route 3 was equal to that of Route 1 (92.41%, the production yield from MCC to P-CNCs).

4. The mass of NH_3 in Route 3 was equal to the mass loss in the curing process.

5. The dialysis process in Routes 2 and 3 were both performed for 5 days, and the water was changed every day, with 800 mL being used

each time.

6. For COD and BOD calculation, the results were calculated by material balance and all organics originated from polymeric cellulose as $(C_6H_{10}O_5)_n$ and urea as $CO(NH_2)_2$, and BOD amount was equal to that of COD produced by cellulose polysaccharides (except the cellulose used for the production of P-CNCs), as urea was degraded by microorganisms without oxygen consumption.

7. The total P and N, NH_3 and Na_2SO_4 contents were all calculated based on material balance.

Notes:

a. P-CNC production process based on pre-phosphorylation (Route 1 of this work):

1. Inventory data of MCC production process from pulp were acquired from reference 11, and CaO was used to neutralize hydrolysates here.

2. The results of the total P and N were measured directly.

3. The calculations of COD and BOD were the sum of the measured values of wastewater and the COD/BOD amount produced by organics.

b. P-CNC production process based on *in-situ* phosphorylation (Route 2 of phosphoric acid hydrolysis):

1. Inventory data were based on the reference 7, and the production yield was regarded as 78%.

c. P-CNC production process based on post-phosphorylation (Route 3 of CNC surface modification in phosphate salt and urea solution):

1. Inventory data were based on the reference 8 and 12, while the raw material was changed from cotton to paper pulp.

Calculation:

1. COD amount of organics was determined by the equation proposed by Wang et al.,[13]

$$m_{COD} = m_{C_6H_{10}O_5} \times 1.185 + m_{CO(NH_2)_2} \times 0.8 \quad (1)$$

which was based on UV-Vis spectrophotometry.

2. For NH_3 calculation in R1,

$$m_{NH_3} = (m_{total\ N} - m_N)/14 \times 17 \quad (2)$$

where $m_{total\ N}$ refers to the total N from $NH_4H_2PO_4$ and urea, m_N denotes the measured total N in the wastewater, 14 and 17 g/mol are the molar masses of N and NH_3, respectively.

3. For the total P calculation in R2,

$$m_{Output\ P} = m_{Input\ P} = m_{H_3PO_4}/98 \times 31 \quad (3)$$

where 98 and 31 g/mol are the molar masses of H_3PO_4 and P, respectively.

4. For the total N calculation in R3,

$$m_N = m_{total\ N} - m_{NH_3}/17 \times 14 \quad (4)$$

where $m_{total\ N}$ refers to the total N from $(NH_4)_2HPO_4$ and urea, m_{NH_3} denotes the mass loss of curing.

Table S3 Input and output data of bleached softwood kraft pulp production (1 g pulp).[14]

Categories			Unit	Value	Background data source
Input	Materials	Logs (dry basis)	cm^3	4.89	Softwood (China); lcacontest-s-unj6@ike-global.com 1.0
		NaOH (30 wt%)	g	0.176	Sodium hydroxide (30%), market average (China); CLCD-China-ECER 0.8
		H_2O_2 (50 wt%)	g	0.019	Hydrogen peroxide (50%), market average (China); CLCD-China-ECER 0.8
		H_2SO_4 (98 wt%)	g	0.017	Sulfuric acid, market average (China); CLCD-China-ECER 0.8
		Na_2SO_4	g	0.022	Disodium sulfate (China); CLCD-China-ECER 0.8
		CaO	g	0.024	Lime production (China); lcacontest-s-85y6@ike-global.com 1.0
		Natural gas	L	0.074	Natural gas (China); CLCD-China-ECER 0.8
		Water	g	44	Tap water (China, industrial); CLCD-China-ECER 0.8
	ClO_2 gen	$NaClO_3$ (available chlorine 15%)	g	0.333	Sodium chlorate (available chlorine 15%) (China); CLCD-China-ECER 0.8
		H_2SO_4 (98 wt%)	g	0.024	Sulfuric acid, market average (China); CLCD-China-ECER 0.8
		CH_4	g	0.005	Methane (China); CLCD-China-ECER 0.8
	Electricity	Softwood kraft pulp production	kW·h	0.350	China power grid transmission (China, to users); display@ike-global.com 0.9
Output	Product	Bleached softwood kraft pulp	g	1	
	CO_2	CO_2-fossil	g	0.171	
		CO_2-biogenic	g	2.209	

HFB	SO_2	g	0.00031
Waste-gas	CH_4	g	0.000028
	N_2O	g	0.000006
Wastewater	Water	g	44
	AOX	g	0.00061
	COD	g	0.051
	Total suspended-solids	g	0.041
	Total dissolved-solids	g	0.2
Waste	Na_2SO_4	g	0.006

Table S4 Selected environmental impact categories.

Impact category	Abbreviation	Unit
Climate change	GWP	kg CO_2 eq/(1 g P-CNCs)
Primary energy demand	PED	MJ/(1 g P-CNCs)
Resource depletion-water	WU	kg/(1 g P-CNCs)
Acidification	AP	kg SO_2 eq/(1 g P-CNCs)
Eutrophication	EP	kg PO_4^{3-}eq/(1 g P-CNCs)
Ecotoxicity	ET	CTUe/(1 g P-CNCs)

Table S5 Prices of materials and energy used for cost calculation.

Materials	Price	Unit	Ref.
Softwood pulp	28000	CNY/ton	15
NaOH (30%)	800	CNY/ton	16
H_2SO_4 (98%)	450	CNY/ton	17
H_3PO_4 (85%)	6800	CNY/ton	18
CaO	900	CNY/ton	19
NaClO	7500	CNY/ton	20
$(NH_4)_2HPO_4$	6500	CNY/ton	21
$NH_4H_2PO_4$	5200	CNY/ton	22
Urea	2800	CNY/ton	23
Water	7.9	CNY/ton	24
Natural gas	5800	CNY/ton	25
Heat	70	CNY/GJ	26
Electricity	0.6768*	CNY/(kW·h)	27

*Classification: General commercial and other electricity consumption (single system) (less than 1kV).

Table S6 Costs of listed materials and energy for per ton of P-CNCs.

Materials/Utilities	R1	R2	R3
Softwood pulp	33656.0	35896.0	60592.0
NaOH (30%)	/	/	35568.8
H_2SO_4 (98%)	8.1	/	7509.6
H_3PO_4 (85%)	/	1481135.2	/
CaO	9	/	/
NaClO	/	/	532.5
$(NH_4)_2HPO_4$	/	/	5739.5
$NH_4H_2PO_4$	1216.8	/	/
Urea	1363.6	/	5619.6
Water	2265.9	23649.4	26681.7
Natural gas	696.0	/	/
Heat	378.8	/	/
Electricity	382392.0	247032	665294.4
Total	421986.2	1787712.6	807538.1

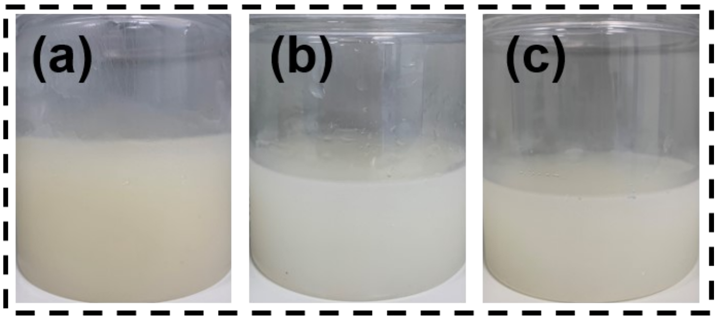

Fig. S1 Photographs of P-CNCs prepared from different molar ratios of MCC/$NH_4H_2PO_4$/urea. (a) 1:0.6:2.4 (b) 1:0.3:1.2 and (c) 1:0.15:0.6.

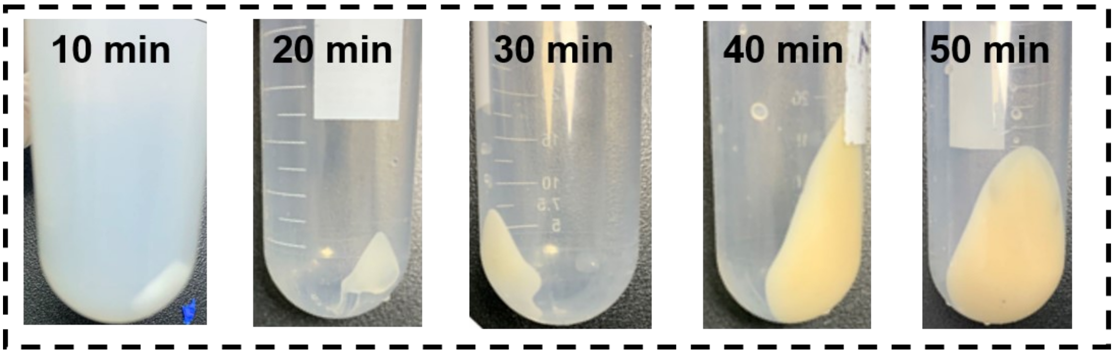

Fig. S2 Residues of P-CNC suspensions after centrifugation prepared from different curing time.

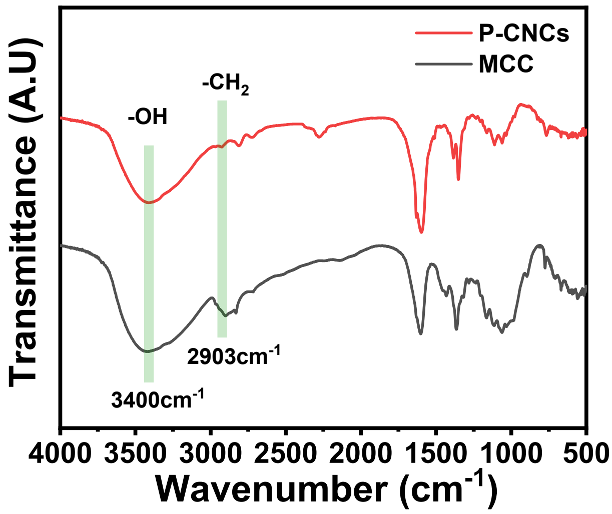

Fig. S3 FT-IR spectra of MCC and P-CNCs.

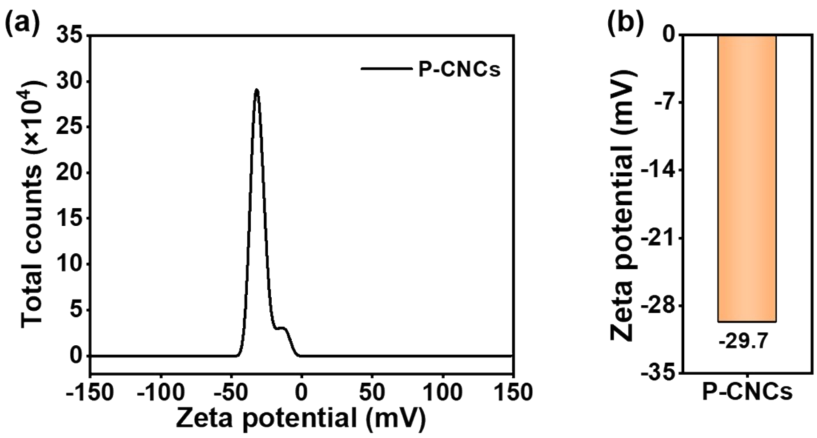

Fig. S4 (a) Zeta potential distribution and (b) zeta potential of P-CNCs.

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