An Environmentally Friendly and Economical Strategy to Cyclically Produce Cellulose Nanocrystals with High Thermal Stability and High Yield

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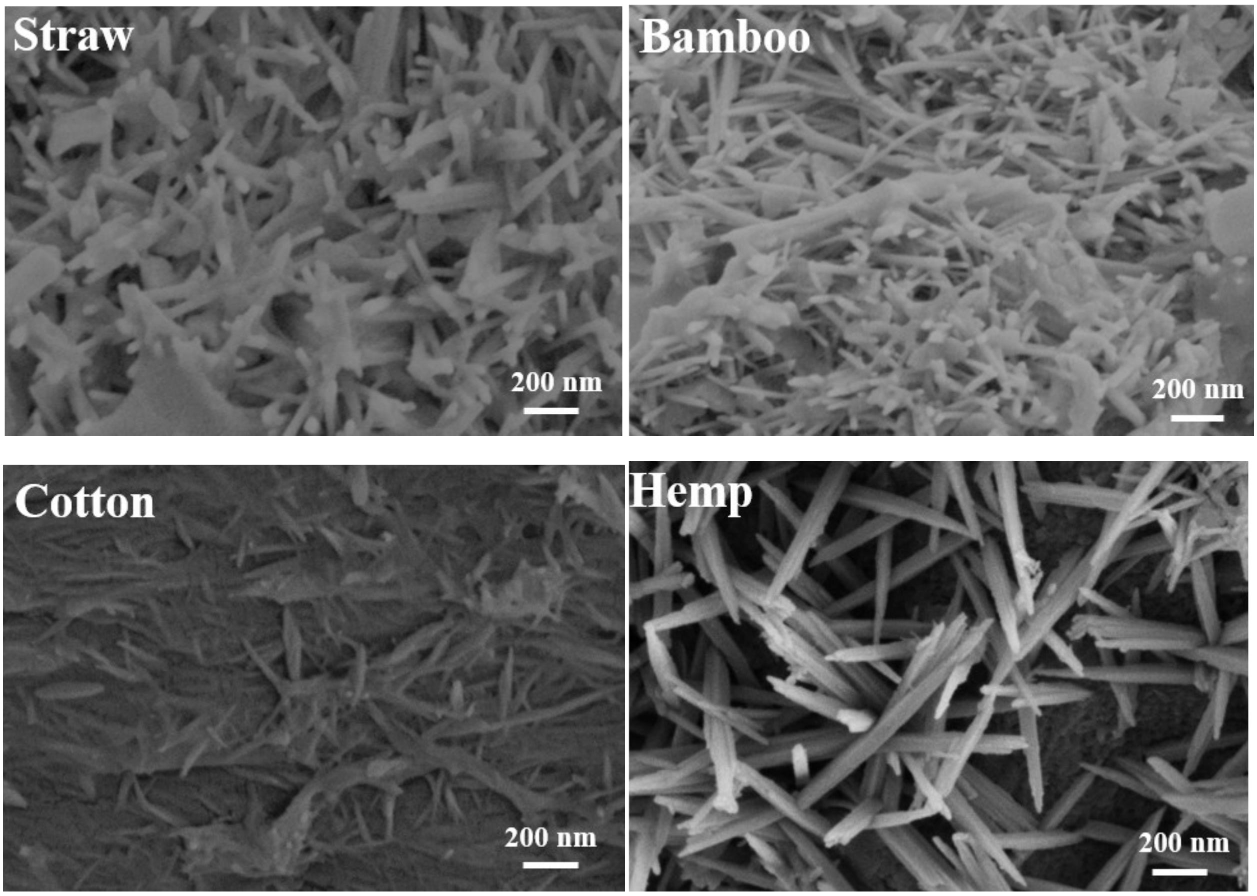

Fig.S1 FE- SEM images of CNC prepared from four kinds of straw, bamboo, cotton and hemp

Tab. S1. The role of ferric chloride in the development of CNC preparation

	Contents	The role played of $FeCl_3$	Report time	Ref.
1	Ferric chloride was introduced into hydrochloric acid hydrolysis to extract cellulose nanocrystals (CNCs) from microcrystalline celluloses (MCC) under hydrothermal conditions.	catalyst	2017	1
2	FeCl3-catalyzed deep eutectic solvent system (F-DES) was invented to fabricate cellulose nanocrystals	catalyst	2019	2
3	Preparation of CNC by FeCl3 Catalysed CA Hydrolysis of MCC	catalyst	2020	3
4	Use ferric chloride to dissolve cellulose	dissolving agent	2020	4

Tab. S2. Comparison of the preparation conditions and properties of cellulose nanocrystals prepared by other method with the cellulose nanocrystals reported in this work.

Raw materials	Preparation conditions	Yield (%)	Crystallinity (%) CNC/raw materials	T_{max} (℃) CNC/raw materials	Disadvantage	Ref.
Commercial microcrystalline cellulose (MCC)	Four inorganic chlorides and HCl	78.6	91.2/83.5	346.3/358.7	Strong acidity of hydrochloric acid requires a lot of water for post-treatment, and hydrochloric acid cannot be recovered.	1
Bleached eucalyptus kraft pulp (BEKP)	$FeCl_3$-catalyzed deep eutectic solvent system (F-DES)	75.8	80.8/75.7	358.2/355.3	The experiment process is complicated.	2
BEKP	$FeCl_3$-catalyzed citric acid	52.0	75.95/67.75	369.3/352.6	Failed to realize the recovery and reuse of experimental solvents.	3
BEKP	Concentrated organic acids	10.3	81.05/76.0	/	Low yield and large environmental pollution caused by organic acids.	5
MCC	2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)	37.2	/	/	Low yield and multiple reaction steps and preparation process had a greater impact on the environment.	6
MCC	Sulfuric acid	54.4	76.9/70,5	245.4/357.5	Low yield and thermal stability, strong acidity of hydrochloric acid requires a lot of water for post-treatment.	7
MCC	Hydrochloric acid	93.7	87.3/76.2	354.5/358.7	Strong acidity of hydrochloric acid requires a lot of water for post-treatment, and hydrochloric acid cannot be recovered.	8
MCC	Hydrogen peroxide (H_2O_2)	/	88.7/77.1	325.3/353.7	Failed to realize the recovery and reuse of experimental solvents.	9
MCC	Recyclable Citric/Hydrochloric Acids	87.0	82.8/70.5	347.3/357.5	Post-processing requires a lot of water.	7
MCC	$FeCl_3$	93.2	75.8/72.7	354.1/347.1	/	This work

Tab.S3 Average Dimensions, Zeta Potential, Carboxyl Contents, Conductometric, T_{max} of CNC_{Fex} and MCC

Sample	[a]Dimensions (nm)		Zeta Potential (mV)	Carboxyl contents (mmol/g)	Conductometric DS	[b]T_{max}(°C)
	length	diameter				
MCC	/	/	/	/		347.1 ± 3.8
CNC_{Fe1}	435 ± 6.2	38 ± 2.6	-21.5 ± 1.3	0.231 ± 0.013	0.038 ± 0.0021	354.3 ± 2.8
CNC_{Fe2}	442 ± 8.9	35 ± 3.8	-20.7 ± 3.5	0.248 ± 0.025	0.040 ± 0.0041	351.1 ± 3.9
CNC_{Fe3}	439 ± 7.6	41 ± 4.8	-20.5 ± 1.2	0.206 ± 0.057	0.033 ± 0.0092	354.3 ± 2.2
CNC_{Fe4}	441 ± 8.3	39 ± 3.3	-22.3 ± 2.8	0.251 ± 0.018	0.041 ± 0.0029	354.1 ± 3.8
CNC_{Fe5}	455 ± 5.1	35 ± 1.8	-20.8 ± 0.9	0.236 ± 0.033	0.038 ± 0.0053	356.7 ± 4.1

[a] *Average length and diameter were obtained by statistics 200 CNC.*

[b] T_{max} was calculated from TGA curves.

Tab. S4 Analysis of variance (ANOVA) of the length and diameter of prepared CNCs

(a)

Anova: Single Factor	length					
SUMMARY						
Groups	Count	Sum	Average	Variance		
Column 1	200	87000	435	132.46231		
Column 2	200	88400	442	154.64322		
Column 3	200	87800	439	342.32161		
Column 4	200	88200	441	388.07035		
Column 5	200	91000	455	642.39196		
ANOVA						
Source of Variation	SS	df	MS	F	$F_{0.05}(dfA, dfe)$	Significance
Between Groups	45440	4	11360	34.219146	2.380875807	*
witin Groups	330318	995	331.97789			
Total	375758	999				

(b)

Anova: Single Factor	diameter					
SUMMARY						
Groups	Count	Sum	Average	Variance		
Column 1	200	7600	38	106.84422		
Column 2	200	7000	35	117.05528		
Column 3	200	8200	41	128.13065		
Column 4	200	7800	39	116.46231		
Column 5	200	6993	34.965	145.75254		
ANOVA						
Source of Variation	SS	df	MS	F	$F_{0.05}(dfA, dfe)$	Significance
Between Groups	3494.921	4	873.73025	7.1122292	2.380875807	*
witin Groups	122234.76	995	122.849			
Total	125729.68	999				

If F> F0.05(*dfA, dfe*), then factor A has a significant influence on the test result, which is indicated by "*";

If F<F0.05(*dfA, dfe*), then the influence of factor A on the test results is not significant, so the "*" sign is not used

Tab. S5 ANVOA of the yield of CNC_{Fex}

Anova: Single Factor	yield					
SUMMARY						
Groups	Count	Sum	Average	Variance		
Column 1	3	282.2	94.066667	1.9033333		
Column 2	3	277.6	92.533333	0.2633333		
Column 3	3	276.3	92.1	0.37		
Column 4	3	282.2	94.066667	0.4433333		
Column 5	3	279.9	93.3	1.27		
ANOVA						
Source of Variation	SS	df	MS	F	$F_{0.05}(dfA, dfe)$	Significance
Between Groups	9.4973333	4	2.3743333	2.7933333	3.478049691	
witin Groups	8.5	10	0.85			
Total	17.997333	14				

If F> F0.05(*dfA, dfe*), then factor A has a significant influence on the test result, which is indicated by "*";

If F<F0.05(*dfA, dfe*), then the influence of factor A on the test results is not significant, so the "*" sign is not used.

Tab. S6 ANVOA of *Xc* of CNC_{Fex}

Anova: Single Factor	X_C					
SUMMARY						
Groups	Count	Sum	Average	Variance		
Column 1	3	228.9	76.3	1.71		
Column 2	3	227.2	75.733333	0.9433333		
Column 3	3	229.7	76.566667	0.2533333		
Column 4	3	224.4	74.8	0.07		
Column 5	3	230.7	76.9	0.43		
ANOVA						
Source of Variation	SS	df	MS	F	$F_{0.05}(dfA, dfe)$	Significance
Between Groups	8.1426667	4	2.0356667	2.9877691	3.478049691	
witin Groups	6.8133333	10	0.6813333			
Total	14.956	14				

If F> F0.05(*dfA, dfe*), then factor A has a significant influence on the test result, which is indicated by "*";
If F<F0.05(*dfA, dfe*), then the influence of factor A on the test results is not significant, so the "*" sign is not used.

Tab. S7 ANVOA of T_{max} of CNC_{Fex}

Anova: Single Factor	T_{max}					
SUMMARY						
Groups	Count	Sum	Average	Variance		
Column 1	3	1062.9	354.3	1.48		
Column 2	3	1053.3	351.1	7.87		
Column 3	3	1062.9	354.3	8.68		
Column 4	3	1062.2	354.06667	4.6633333		
Column 5	3	1070	356.66667	3.4233333		
ANOVA						
Source of Variation	SS	df	MS	F	$F_{0.05}(dfA, dfe)$	Significance
Between Groups	47.004	4	11.751	2.2497128	3.478049691	
witin Groups	52.233333	10	5.2233333			
Total	99.237333	14				

If F> F0.05(*dfA, dfe*), then factor A has a significant influence on the test result, which is indicated by "*";

If F<F0.05(*dfA, dfe*), then the influence of factor A on the test results is not significant, so the "*" sign is not used.

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