Supplementary Information

Ultrafast and Energy-saving Extraction of Cellulose Nanocrystals

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Materials

Cotton pulp with cellulose polymerization degree (DP) of 600 was supplied by Silver Hawk Co. Ltd. (Gaomi, China), the content of cellulose in cotton pulp is 96.2 wt%. Ammonium persulfate (APS, 99 wt%) was purchased from Aladdin Chemical Reagent Corp. Potassium iodide (KI, 99.5 wt%), sodium bicarbonate ($NaHCO_3$, 99.7 wt%), methanol (99.7%) and tert-butyl alcohol (99.0 %), sodium hydroxide (NaOH, 96 wt%), hydrochloric acid (HCl, 36.5 wt%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used for all experiments.

Preparation of CNCs *via* NaOH granules activated ammonium persulfate oxidation.

Some parameters, such as initial temperature, reaction time and NaOH concentration were evaluated to find the optimal conditions for the efficient preparation of CNCs. 5 g of pulp soaked in 200 mL 0.13 mol/L APS solution and heated to 50 °C. Certain quantity of APS and NaOH granules were successively added to the mixture solution to trigger the reaction. After vigorous stirring for designed times (1, 2, 3, 6, 9, 12, 15 minutes), the sample was diluted 5-fold with deionized water for ending the reaction. To facilitate the collection CNC suspension, the suspension was ultrasonically smashed using an ultrasonic cell disrupter (20 kHz, 180 W) for 1 minute during centrifugation. The impurity was removed by reiterative centrifugation at 8000 rpm for 10 minutes, until the most of the CNCs were converted to suspension. The CNCs suspension with a conductivity of 78.3 μS/cm and a concentration of 1.5wt% was prepared. The yield of the CNCs was calculated as the weight percentage of the dried CNCs to the pulp feedstock. The total solid was calculated as the weight percentage of the pulp after hydrolysis to the pulp feedstock.

Characterizations

The Fourier transform infrared spectroscopy (FT-IR) spectra were collected from 4000 to 400 cm^{-1} for 32 scans at a resolution of 2 cm^{-1} using a Bruker VERTEX 70 spectrometer. Before the testing, the CNCs suspension was adjusted to acidic and freeze-drying. The dried CNCs were

ground with KBr and pressed into transparent flakes. The spectra of the samples were obtained in transmission mode.

The thermal stability of CNCs-COOH were carried out using TA Instruments Q500 thermogravimetric analyzer under a nitrogen atmosphere. The temperature was set from 40 °C to 600 °C with a heating rate of 10 °C min^{-1} to record the TGA analysis curves.

The UV-vis absorption spectra were carried out in the range of 200-500 nm to evaluate the residual amount of APS. The calibration curve of APS concentration was conducted by the methods reported by Liang et al.[1]

Raman spectra were collected on a Horiba/Jobin Yvon laser Raman analyzer LabRAM HR 800 (Horiba/Jobin Yvon, Longjumeau, France) equipped with a diode 784.8 nm laser, operating at 1000 μm. The supernatant under different reaction conditions was taken in a glass dish for testing.

Atomic force microscope (AFM) images were acquired using a Dimension lcon (Bruker, USA) under the peak force tapping mode. For AFM measurement, a drop of CNCs suspension (0.1 mg/mL) was spin-coated on freshly cleaved mica at 2000 rpm for 1 minute.

X-ray diffraction (XRD) measurement was performed on a rigaku SmartLab diffractometer equipped with Cu Kα radiation (λ =0.154 nm) in the diffraction angle (2θ) range from 5° to 40° with a step interval of 0.02° and a scanning rate of 5° min^{-1}. The crystallinity of CNCs was calculated using the following equation [2]:

$$C_I = \frac{I_{200} - I_{am}}{I_{200}} \times 100\% \qquad (1)$$

The Zeta potential of the CNCs were measured on a Malvern Nano ZS90 light scattering instrument at a concentration of 0.01 mg mL^{-1} with a Zetasizer analyzer. Deionized water was used as a dispersant.

Inductively coupled plasma mass spectrometry (ICP-MS) were recorded using a Aglient 7850 analyzer calibrated with a standard solution. Sample (5.78 mg) was digested in a small amount of concentrated nitric acid (5 mL) by heating at 110 °C for 1h. After that, the liquid was obtained by filtration and then

diluted to a final volume of 15 mL with H_2O. The final solution was used for the ICP-MS analysis of the concentration of Cu, Mn and Fe ion.
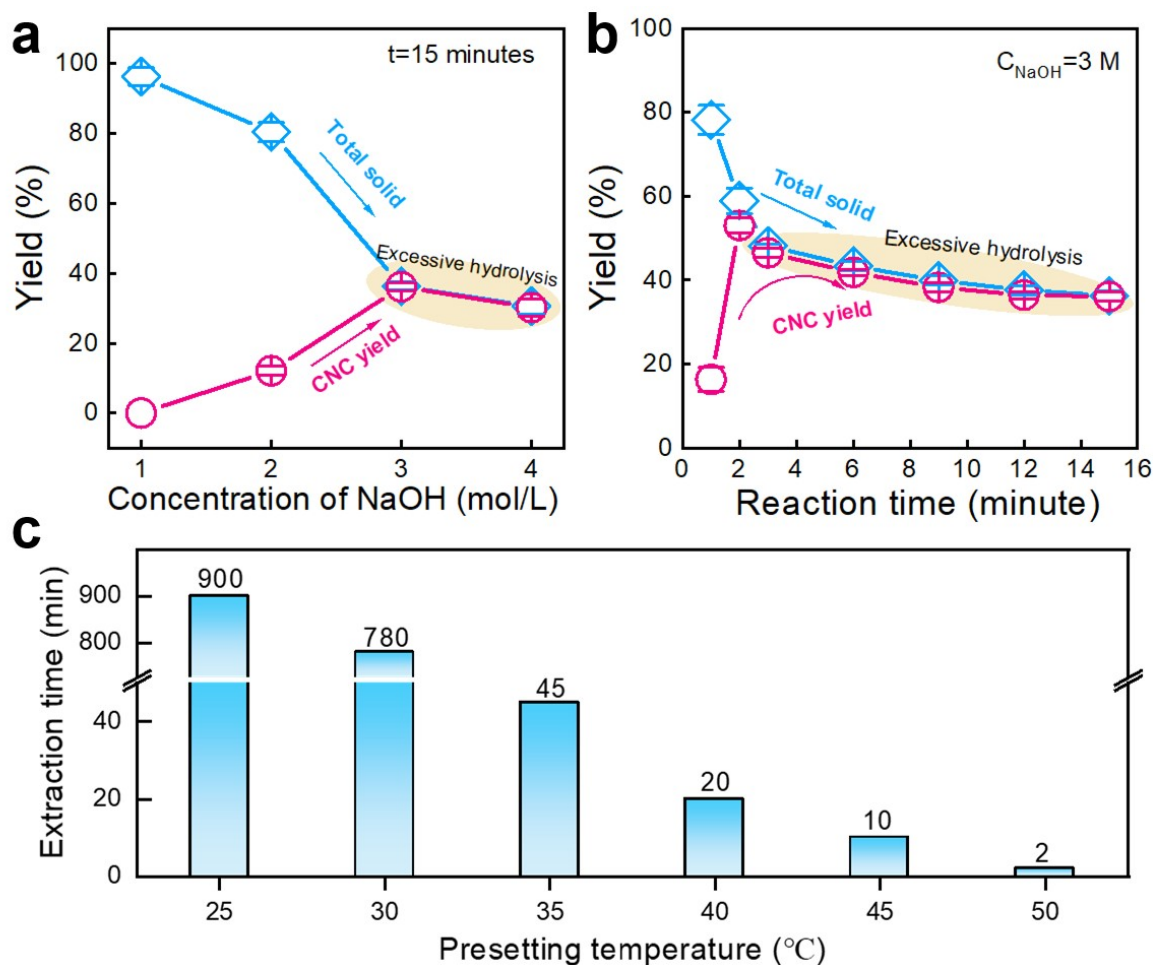
Fig. S1 Effect of NaOH concentration (a) and reaction time (b) on CNCs yield and total solid. The minimum preparation time of CNCs at different presetting temperatures (c).

The effects of NaOH concentration on CNCs yield and total solid were studied. When the NaOH concentration is 1 M, almost no CNCs were extracted in 15 minutes. In this case, the total solid reached 94.47%, indicating that the pulp was hardly hydrolyzed. The CNCs yield reached the highest (36.12%) when the NaOH concentration was 3 M. With the further increase of NaOH concentration to 4 M, both total solid and CNCs yield was decreased, illustrating the excessive hydrolysis of pulp. Shortening the reaction time is an effective way to avoid excessive hydrolysis of pulp and improve the yield of CNCs. Therefore, the effect of reaction time on CNCs yield at NaOH concentration of 3 M was researched (Fig. S1b). It is obvious that the rapid reduction of total solid happened within the first 3 minutes and nearly 52 wt.% of pulp was hydrolyzed to soluble products. After that, the hydrolysis of pulp became much slower. This statement should be attributed to the fast degradation of the amorphous cellulose area by the

high concentration of oxidant at the beginning. The yield of CNCs appears the tendency of increased first and then decrease with the extension of reaction time, and the yield reached the maximum at 2 minutes (53.04%). When the reaction time is more than 2 minutes, the total solid and CNCs yield decrease simultaneously, demonstrating that the pulp was excessively hydrolyzed in a short reaction time. By adjusting the presetting temperature, the preparation efficiency of CNCs can be regulated to alleviate the excessive hydrolysis of pulp. When the preset temperature rises from 35 ° C to 50 ° C, the preparation time of CNC is 45, 20, 10 and 2 minutes respectively
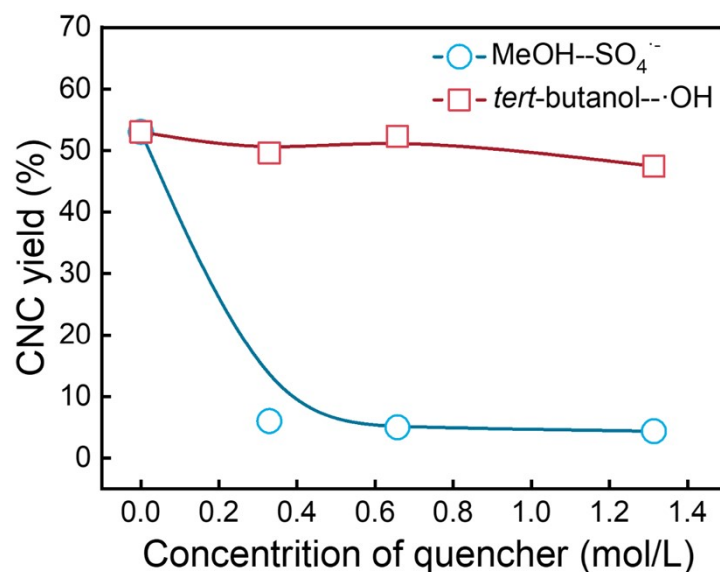
Fig. S2 Effect of free radical quencher on CNCs yield. Methanol and *tert*-butanol are radical scavengers for $SO_4^{\bullet-}$ and $\bullet OH$, respectively.

In our CNCs extraction system, there are two strongly oxidizing free radicals $SO_4^{\bullet-}$ and $\cdot OH$, which are formed by decomposition of APS and Fenton reaction, respectively. The radical quenching experiments were applied to identify the type of free radicals produced in the NaOH granules activated APS oxidation system. When methanol or tert-butanol (TBA) (radical scavenger for $SO_4^{\bullet-}$ and $\bullet OH$, respectively) was added into the reaction systems, the CNCs yield was decreased from 53.04% to 4.38% and 47.46%, respectively. Implying that the $SO_4^{\bullet-}$ is the major radical in the extraction of CNCs.

Table S1. ICP-MS data of pulp.

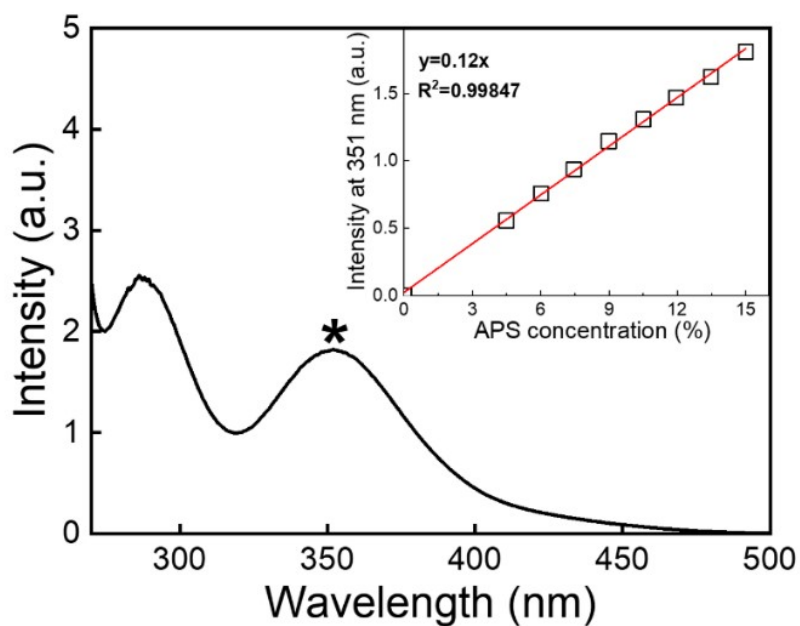| Element	Content (ppm)
Cu	21.44
Mn	83.90
Fe	415.16

Fig. S3 UV-vis absorption spectra and standard curve of APS/NaHCO$_3$/KI solutions

The measurement of APS residue is based on the method established by Liang et al.[1] In detail, 0.225 g NaHCO$_3$, and 4.5 g KI were into 45 mL deionized water in 50-mL glass vials. 5 μL of reaction supernatant was added subsequently. The resulting solutions were shaken and allowed to equilibrate for 10 minutes. The APS reacts with KI and forms an iodine yellow color that absorbs in the UV-Vis range with maximum absorptions at 288 and 352 nm. The intensity of absorption peak at 351 nm was used to measure the APS residue in the reaction system.
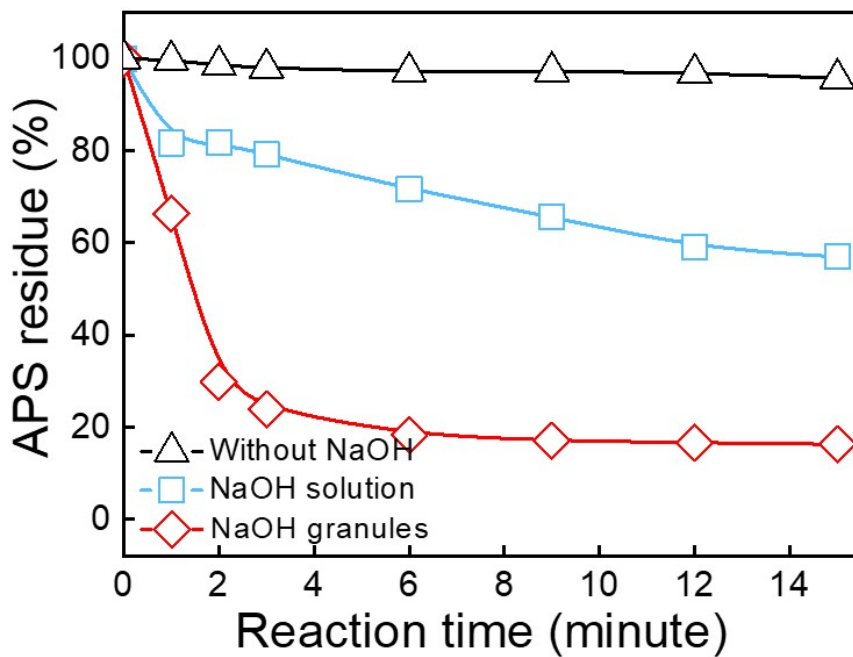
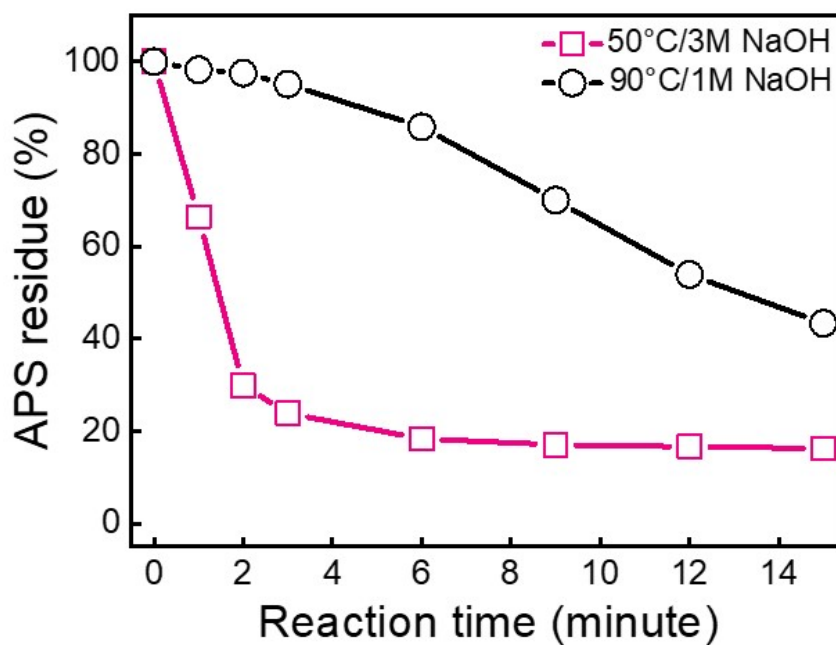Fig. S4 Effect of NaOH addition method on APS residue.

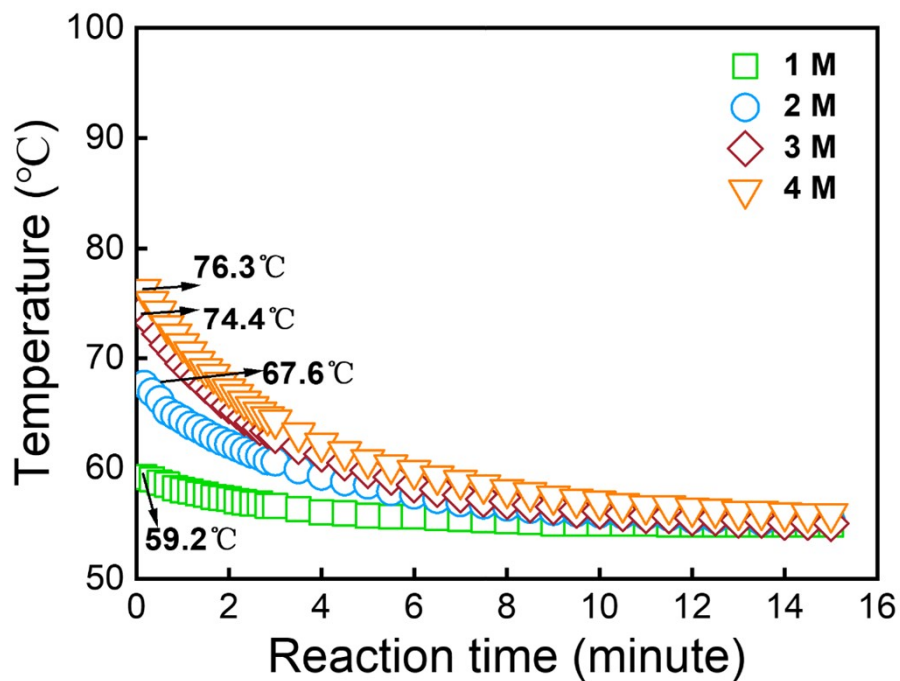Fig. S5 Effects of NaOH concentration and temperature on APS residue.

Fig. S6 Effect of NaOH concentration on temperature of water. The presetting temperature is 50 °C.
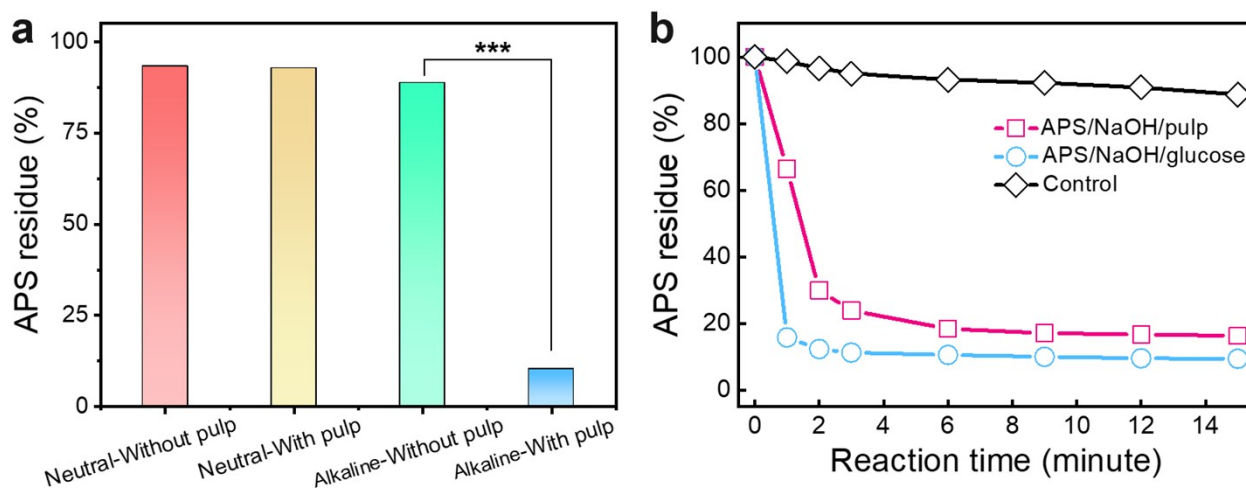

Fig. S7 (a) Effect of pulp and alkali on APS residue. (b) Comparison of effects of pulp and glucose on APS residue. (NaOH concentration is 3 M, APS/NaOH/water as the control experiment)
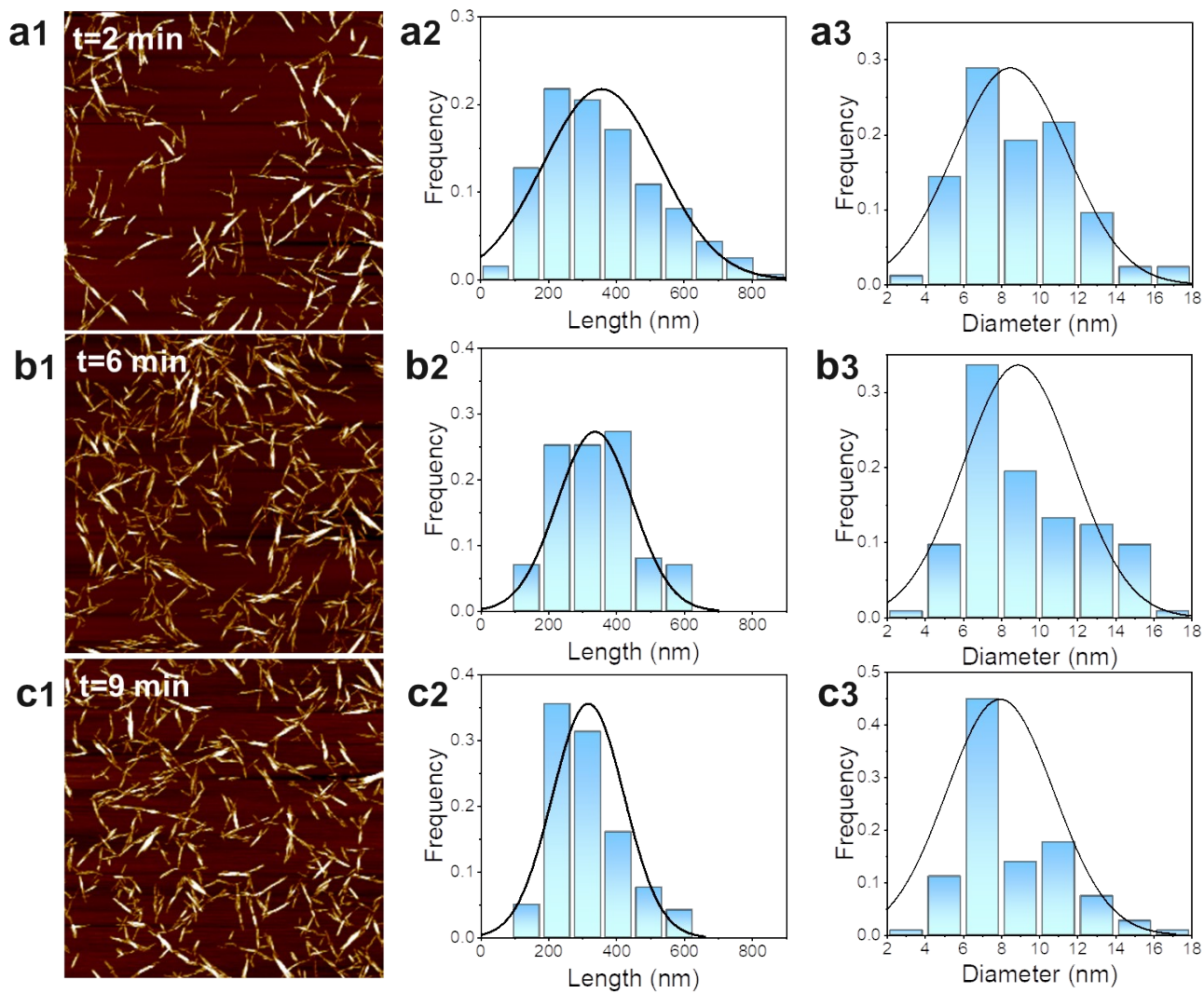
Fig. S8 Atomic force microscope height images and the size statistics of CNCs prepared in (a) 2, (b) 6, and (c) 9 minutes.
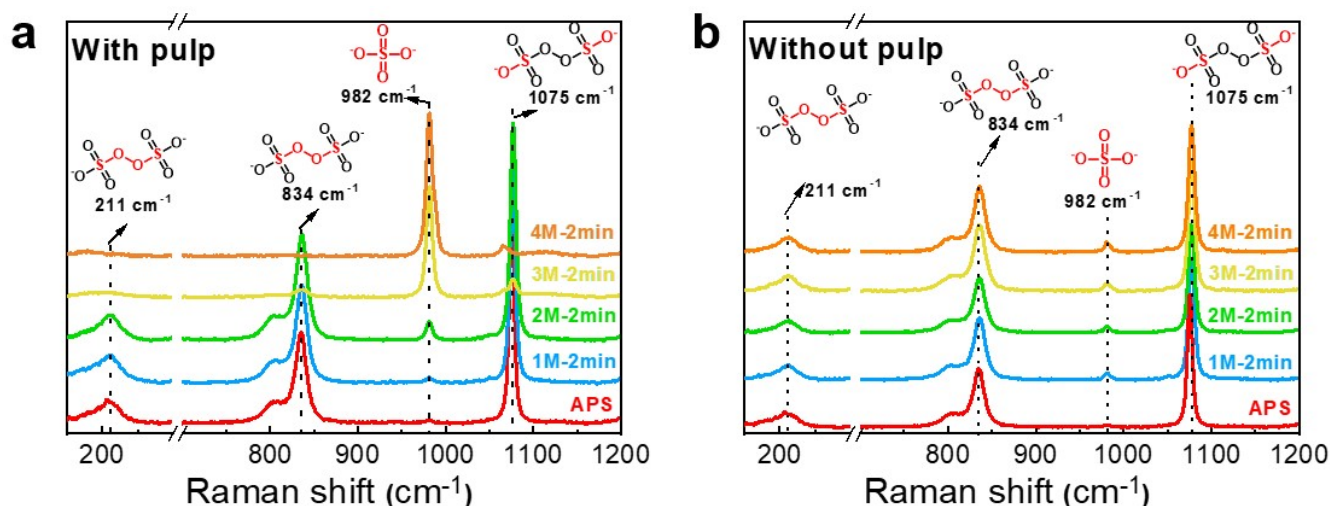
Fig. S9 Raman spectra of supernatants in CNCs preparation systems under different NaOH concentrations.

APS exhibit three major Raman peaks: 211 cm^{-1} (δm: S-O-O-S bridge), 834 cm^{-1} (νm: S-O-O-S bridge), and 1075 cm^{-1} (νs: S-O bond of the SO_3^- group of the persulfate anion). The peroxide bond of APS breaks under the combined action of NaOH, APS and cellulose, and subsequently generates two SO_4^{2-} (exhibits a $\nu_1(SO_4^{2-})$ band at 982 cm^{-1}).[3] With the increase of NaOH concentration, the Raman peaks of APS began to diminish as the O-O bond of the persulfate cleaved. When the NaOH concentration increased to 3 M, the peak at 982 cm^{-1} increased sharply, and the peaks attributed to APS were almost invisible. Therefore, the by-product of APS decomposition is mainly harmless sulfate. In the absence of pulp, the Raman characteristic peak of persulfate has no obvious change, indicating that persulfate has almost no decomposition.
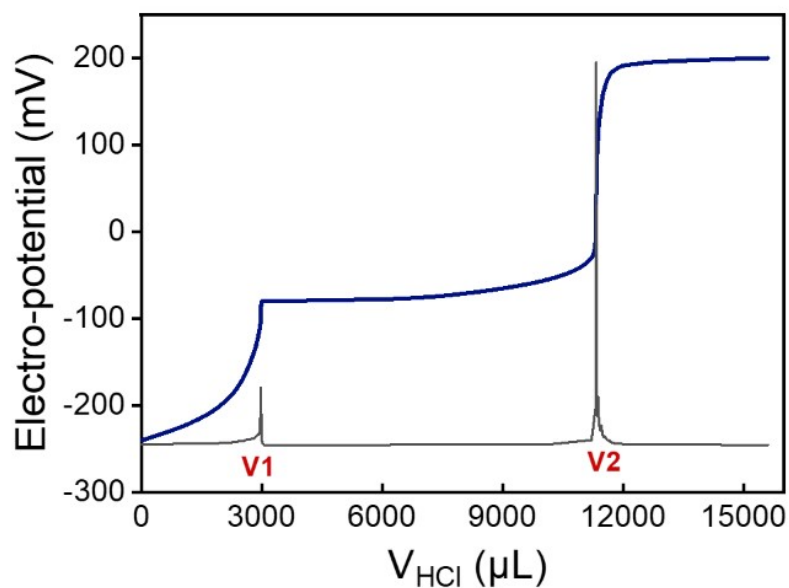
Fig. S10 Electro-potential titration curves of CNCs.

The carboxyl group content of CNCs was determined via potentiometric titration. The electro-potential was measured using a PHS-3E meter (Leici, China). In brief, 20 mL of a 0.5 wt% CNCs suspension was adjusted electro-potential to ~-220 mV using 0.1 M NaOH solution. The CNCs suspension was then titrated with 0.01 M amount of HCl, and the carboxyl contents were calculated from the resulting electro-potential curves. The carboxyl groups content (mmol/g) of the sample was calculated based on the following equation:

$$[\text{-COOH}] = (V_2 - V_1)C_{HCl}/m_{CNCs} \tag{4}$$

Table S2 Calculation of energy-consumption and time-consumption for different CNCs preparation method.

	Stirring			Heating			Probe sonication		
	P (W)[a]	TC (h)[b]	EC (kJ) [c]	P (W)	TC (h)	EC (kJ)	P(W)	TC (h)	EC (kJ)
Sulfuric acid hydrolysis	100	0.75	270	500	0.75	1350	-	-	-
APS oxidation	100	6	2160	500	6	10800	-	-	-
Tempo oxidation	100	4.5	1620	-	-	-	300	1	1080
This work	100	0.033	11.88	500	0.033	59.4	180	0.028	18.14

[a]P means Power,
[b]TC means time consumption,
[c]EC means energy consumption.

Table S3 Calculation of total energy-consumption and time-consumption for different CNCs preparation method.

	Mass of raw material (w/v%)	Total energy consumption (kJ)	Yield (%)	Mass of obtained CNCs (g)	Total time consumption (h)	Energy efficiency (g/kJ)	Conversion rate (g/h)
Sulfuric acid hydrolysis	5	1620	41.7	2.085	0.75	1.287×10^{-3}	2.78
APS oxidation	10	12960	65	6.5	6	5.015×10^{-4}	1.08
Tempo oxidation	3	2160	70	2.1	5	9.722×10^{-4}	0.42
This work	5	89.42	53.14	2.657	0.061	3×10^{-2}	43.56

References

1. C. Liang, C. F. Huang, N. Mohanty and R. M. Kurakalva, *Chemosphere*, 2008, 73, 1540-1543.
2. L. Zhou, N. Li, J. Shu, Y. Liu, K. Wang, X. Cui, Y. Yuan, B. Ding, Y. Geng, Z. Wang, Y. Duan and J. Zhang, *ACS Sustainable Chem. Eng.*, 2018, 6, 12403–12410.
3. E. Lam, A. C. W. Leung, Y. Liu, E. Majid, S. Hrapovic, K. B. Male and J. H. T. Luong, *ACS Sustainable Chem. Eng.* 2013, 1, 278−283.