Supporting Information

Structure Selectivity of Alkaline Periodate Oxidation on Lignocellulose for Facile Isolation of Cellulose Nanocrystals

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Author Contributions

Materials

Microcrystalline cellulose powder (MCC) with an average particle size of 50 µm, periodic acid (H_5IO_6), and deuterium oxide (D_2O, with 99.9 atom % D) were bought from Sigma-Aldrich. Aqueous hydrochloric acid (HCl, 37%), potassium hydroxide (KOH), potassium phosphate (K_3PO_4) potassium carbonate (K_2CO_3), sodium periodate ($NaIO_4$) and sodium hydroxide (NaOH) were purchased from VWR. All chemicals were of analytical grade or higher. Deionized water (DI water) was used throughout the experiments. The wood pulp from beech was a gift from Lenzing (Austria), the sawdust (of Scots pine (*Pinus sylvestris*) and European beech (*Fagus sylvatica*)) was from own workshop, and kenaf and flax fibers were received as gift from own faculty.

Periodate oxidation for the preparation of cellulose nanocrystals (PO-CNCs) from lignocellulose

A certain amount of H_5IO_6 was added into reaction bottle with DI water and the pH of these mixtures were adjusted to the desired value by using KOH (or K_2CO_3 and K_3PO_4). 1 g of lignocellulose was added into the reaction and the total volume of reactions was fixed to 150 mL. The reactions were performed at various temperatures under continuous stirring in dark. Immediately after the reaction, the solid parts were collected via centrifugation (14000 rpm, 20 min, 4 °C, on Thermo scientific Multifuge X3 FR, F15-6•100y). Then, the solid was re-suspended in DI water, and 5 mL of ethylene glycol was added before the suspension was treated with ultrasonication (Elmasonic P 30 H, 37 kHz, 180 W) for one hour in ice-cold water. Thereafter, the solid product were thoroughly purified via dialysis in water using the dialysis membrane with a molecular-weight cut-off of 10000 Da (Thermo Fisher Scientific) and the volume of the obtained PO-CNCs suspension were fixed at 100 mL. The remained stable PO-CNCs in supernatant after 20 min centrifugation at 3000 rpm (25 °C) were used for yield calculation and further characterization.

Recycling of periodate with ozone

An oxygen-based ozone generator (Sander Laboratory Ozonizer 301.19) with 30 g/hour of ozone concentration in the gas phase was used. The ozone treatment was performed

in a 250 mL glass bottle with a three-way dispenser. At the beginning, the ozone generator was equilibrated under oxygen flow for 10 min before the ozone gas stream was switched on. Then, the ozone-containing gas was purged at a constant flow through a glass pipe into the solution under vigorous stirring for at least 1 hour. After that, the solution was purged with O_2 gas to remove remained O_3[1].

Preparation of $K_4H_2I_2O_{10} \cdot 8H_2O$ from periodate solution at pH 10

7.04 g of H_5IO_6 was dissolved in DI water and the pH value was adjusted with aqueous KOH solution (4 mol/L) to 10±0.05 in a total 150 mL solution. This solution was put in a fridge at 4 °Cover night, leading to crystals. The structure was determined using X-ray crystallography (see below for details).

Characterizations

Transmission electron microscopy (TEM)

Dried PO-CNCs were also characterized with TEM, and the samples were prepared from its suspension in water of 0.01 wt.%. The TEM observation was performed on a CM 12 Transmission Electron Microscope (Philips, Netherland). The specimens were stained by phosphotungstic acid solution (2 wt.% in water) and the pH value was adjusted to 7.0 using aqueous NaOH of 1 mol/L.

Atomic Force Microscopy (AFM)

AFM scans in height and amplitude mode were carried out via Tapping Mode in air on a Cypher 5E (Asylum Research) using proprietary silicon cantilevers with a tip radius of 7 nm, a spring constant of 2 N/m, and a resonance frequency of 70 kHz. The PO-CNCs samples were prepared on cleaned wafer using their aqueous suspensions of 0.01 wt.%. Obtained images were processed with Gwyddion (Free Software Foundation, Inc., Boston, USA).

Liquid-state ^{1}H-NMR, ^{13}C-NMR spectroscopy and attached proton test (APT)

The isolation of PO-CNCs from MCC was performed in D_2O. 1.76 g of H_5IO_6 was dissolved in D_2O and the pH of reaction solution was adjusted to 10 by KOH (4 mol/L) which was dissolved in D_2O, 0.25 g of MCC was added into the solution and the total volume of reaction were fixed to 38 mL. The reaction was performed at room temperature under continuous stirring for 14 days in dark. Immediately after the reaction, the solid were separated out with centrifugation (14000 rpm, 20min, 4 °C, Thermo scientific Multifuge X3 FR, F15-6•100y), then the supernatant was filtered for liquid-state ^{1}H-NMR, ^{13}C-NMR, and APT measurement. All spectra were obtained on a Bruker 300 MHz NMR spectrometer, a Bruker Avance III 500 MHz spectrometer or a Varian Inova 600 MHz spectrometer in D_2O at 25°C. Chemical shifts are reported relative to the solvent peak.

Solid-state ^{13}C CP/MAS NMR spectroscopy

The experiments were run on a Bruker 850 MHz spectrometer equipped with a 3.2 mm MAS Efree probe. All HC-CP spectra were recorded at a spinning frequency of 11 kHz and a temperature at 287 K. The proton to carbon CP transfer time of 2ms and inter-scan delay (d1) of 4 seconds were kept constant between different measurements. During CP, a ramped pulse (100 to 90 percent) was applied on the proton channel. A total of 16384 scans were acquired for each sample.

Determination of contents of aldehyde groups by titration

Before the titration, the pH value of the aqueous PO-CNCs suspension was adjusted to 3.5 using HCl solution (1 mol/L). Then, 10 mL hydroxylamine hydrochloride solution (5% w/w) was added into the suspension. The pH of the solution was kept at 3.5 by adding NaOH solution (0.05 M), until no decrease of pH was observed. The contents of aldehyde groups were calculated based on the consumption of the aqueous NaOH solution according to:

$$C = \frac{C_{NaOH}V_{NaOH}}{m} \qquad (1)$$

where C is the concentration of aldehyde groups on PO-CNCs, C_{NaOH} is the concentration of the aqueous NaOH solution, V_{NaOH} is the volume of the used NaOH solution, and m is the mass of dried PO-CNCs[2].

Determination of contents of aldehyde groups by elemental analysis

The amount of aldehyde groups was determined based on the Schiff base formation between aldehyde groups and hexylamine by measuring the mass ratio of carbon and nitrogen. 0.14 g of purified sample were transferred into methanol by repeated washing with methanol and collecting with ultracentrifuge. Then, 0.5 mL of hexylamine was added into the suspension and the mixture was stirred for 4 hours. After that, 0.5 g NaBH$_4$ was added into the mixture and the mixture was stirred for overnight. After the reaction, the product was repeatedly washed with ethanol and water, and finally dried in vacuum dryer at 60 °C. The contents of carbon, hydrogen and nitrogen were determined on an Elemental Analyser 4.1 vario EL III (Elementar, Germany).

Determination of carboxyl groups by conductivity titration

Before the titration, the pH value of the PO-CNCs suspension was adjusted to 2 using aqueous HCl solution of 1 mol/L. Then, the suspension was titrated on 665 Dosimat (Metrohm) employing a dosing rate of 0.01 mL/s, where the conductivity was recorded using the 865 Conductivity Module (Metrohm) with an interval of 2 s.

The contents of carboxyl groups were calculated based on the consumption of the aqueous NaOH solution for carboxylic groups according to:

$$C = \frac{C_{NaOH}V_{NaOH}}{m} \qquad (2)$$

where C is the content of carboxyl groups, C_{NaOH} is the concentration of the aqueous NaOH solution (0.05 mol/L), V_{NaOH} is the volume of the used NaOH solution for neutralizing carboxylic groups and m is the mass of PO-CNCs[3].

Zeta Potential

Zeta Potential measurement was performed on a Zetasizer Nano ZS (Malvern Instruments Ltd., UK). For the Zeta potential measurement, the PO-CNCs suspensions

were diluted to a concentration of ~0.5 mg/mL with DI water. 1 mL of PO-CNCs suspension in DTS1070 disposable folded capillary cell was used for the measurement.

Raman Spectroscopy

Raman spectra were measured using a HORIBA Scientific LabRAM HR 800 (400-1100 nm) spectrometer with open-electrode CCD detector and a confocal pinhole with user controlled variable aperture, in combination with a free space optical microscope and a He:Ne laser (632.8 nm).

X-ray crystallography

Crystal data and details of the data collections are given in Table S3. X-ray data were collected on a STOE IPDS II diffractometer (graphite monochromated Mo-Kα radiation, λ = 0.71073 Å) by use of ω scans at -140 °C. The structure was solved with SHELXT and refined on F^2 using all reflections with SHELXL-18[4]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined freely. Face-indexed absorption corrections were performed numerically with the program X-RED[5]. The structure of $K_4H_2I_2O_{10} \cdot 8H_2O$ has been reported previously, with slightly different cell parameters[6].

Analysis of chemical compositions of various lignocelluloses

The samples were shredded to a size of averagely 0.5 mm before applying the extraction on these various lignocelluloses with toluene. The dry contents of the extracted and non-extracted sample were determined. The content of lignin was detected according to the method from Klason[7] and the content of cellulose was detected according to Kürschner's method[8]. $NaClO_2$ was used for the determination of holocellulose[9]. The ash content was determined using thermogravimetric analysis at 600 °C. All measurements were performed at least as duplicate measurements.
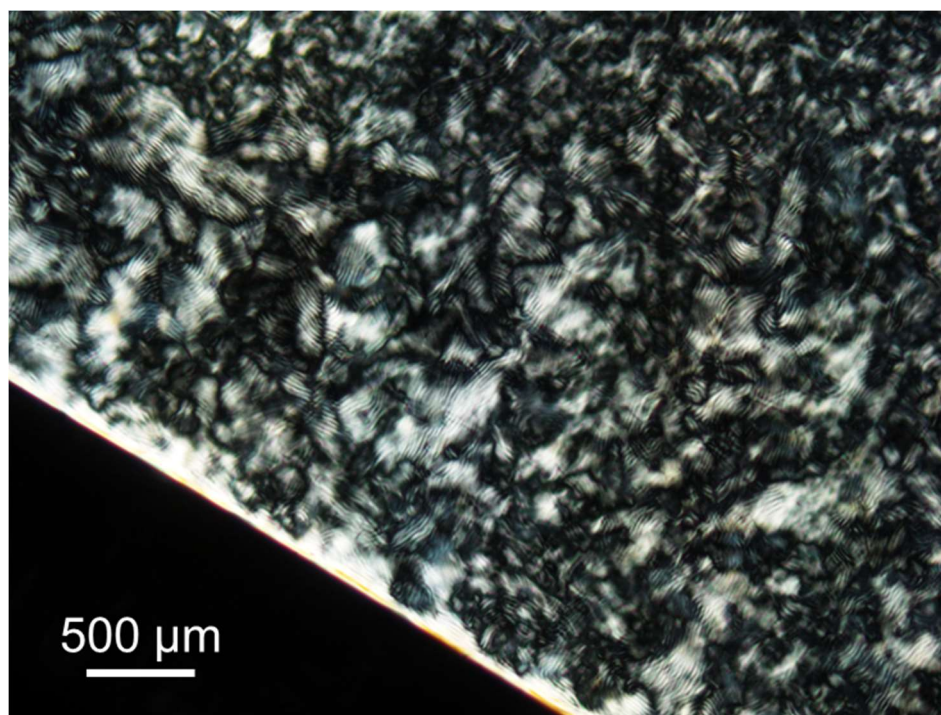
Supplementary Text

Figure S1. Polarized optical microscopy image of PO-CNCs suspension (3 wt.%) showing a typical fingerprint pattern of the cholesteric phase in a confined geometry (Square quartz tube, inner size: 2mm*1.5cm*4cm).
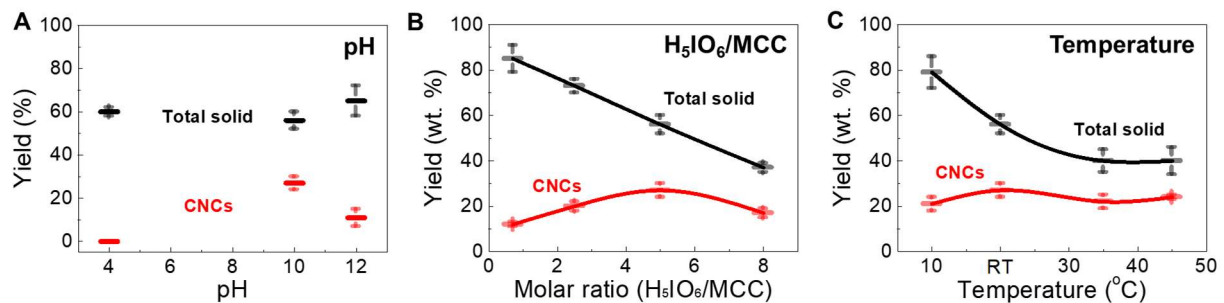

Figure S2. Effect of various reaction parameters on the isolation process. A) pH value of reaction solution. B) The molar ratio of periodate and MCC. C) Temperature.

In this work, we examined the effect exerted by changing the pH value, the amount of periodate, and temperature in addition to the other parameters presented in main text.

In order to find the optimal reaction pH, the isolation was operated with a molar ratio of 5 mol periodate per 1 mol anhydroglucose units of cellulose at room temperature for 14 days. The reaction was performed at pH 4 using sodium periodate for oxidation. Because of the low solubility of sodium and potassium periodate salts at the pH value between 6 and 9, the reaction in this pH range was not successful.

In order to find the optimal amount of periodate, the isolation was operated at room temperature for 14 days, and periodate oxidation performed at pH 10 on MCC.

In order to find the optimal reaction temperature, the isolation was operated with a molar ratio of 5 at pH 10 for 14 days.

Table S1. Separation of all possible PO-CNCs from total solid after various reaction times via centrifugation.

Sample name	Total solid[a]	1st centrifugation		2nd	3rd	4th	5th	6th	Total PO-CNCs[a]
		PO-CNCs[a]	Sediment[a]			PO-CNCs[a]			
10 days	59	20	39	3.6	2	1.1	0	0	26.7
14 days	56	27	29	4.5	4.5	2.8	1.3	0	40.1
30 days	50	35	15	4.1	2.8	0.8	0	0	42.7

a: the data unit is wt.%

The sediment obtained from first centrifugation on total solid was re-suspended in 100 mL DI water. This suspension was treated with centrifugation at 3000 rpm for 20 min at 25 °C. The remained PO-CNCs in supernatant were collected and used for the calculation of yield. This separation process was repeated 5 times until no CNCs were found in the supernatant. The total yield of PO-CNCs from 10, 14 and 30 days reaction reached 26.7 wt.%, 40.1 wt.% and 42.7 wt.%.
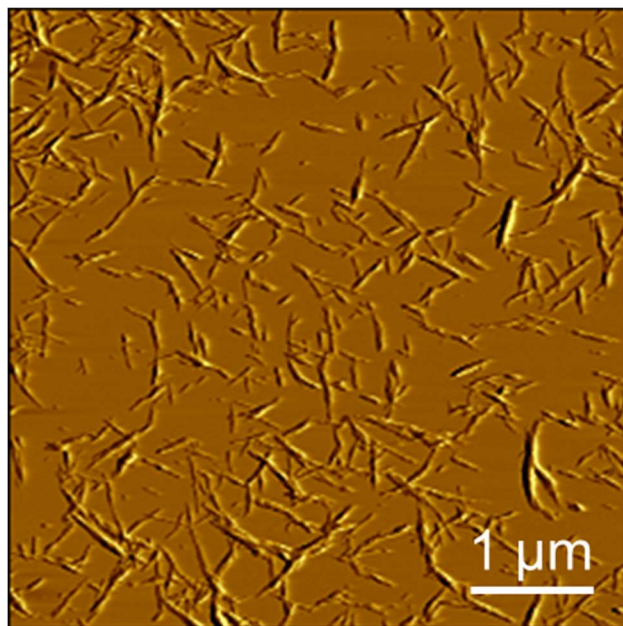
Figure S3. A representative AFM image of PO-CNCs from 14 days reaction.
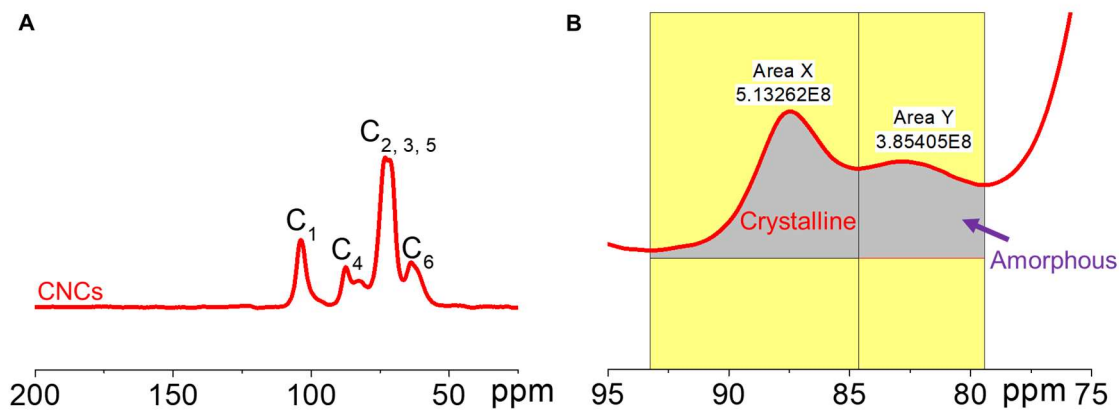
Figure S4. Solid-state ^{13}C CP/MAS NMR spectrum for the determination of crystallinity index of PO-CNCs (from 14 days reaction).

The crystallinity index of the PO-CNCs was calculated based on the solid-state ^{13}C NMR spectra (Figure S4). The area of individual peaks attributed to C4 within ordered (crystalline) and non-ordered (amorphous) regions were extracted by an integrate process using Origin 16. Then, the crystallinity index was calculated using the following equation:[10]

$$\text{Crystallinity (\%)} = \frac{X}{X + Y} \qquad (3)$$

In this equation, X and Y represent the areas under the curves as shown in Figure S4B.

Based on the areas under the signals ascribed to C4 in PO-CNCs, the crystallinity index was calculated to be around 57.1%.
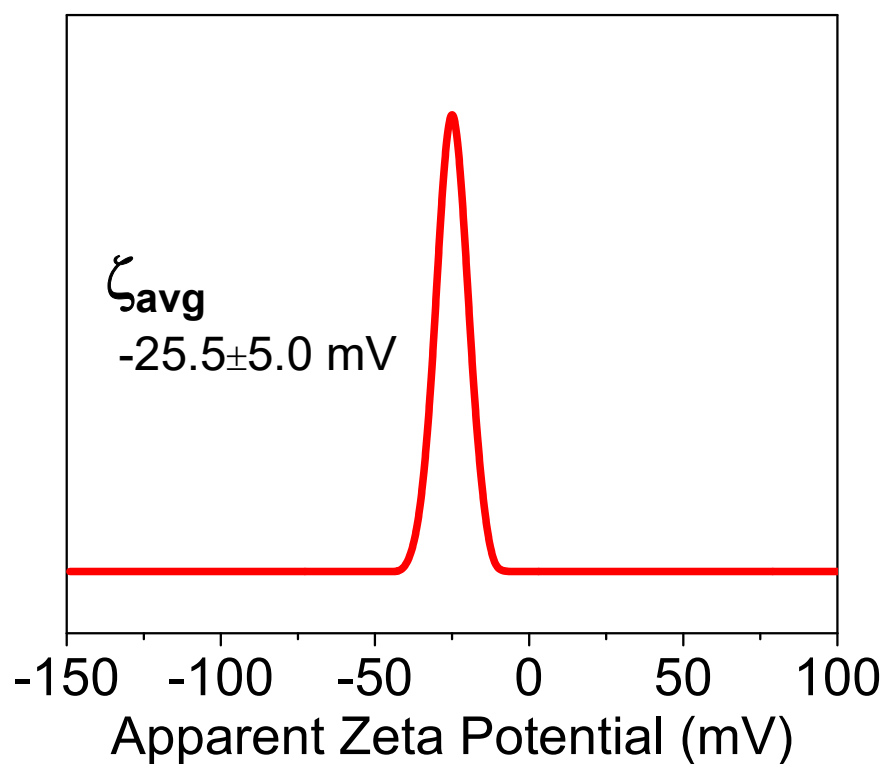

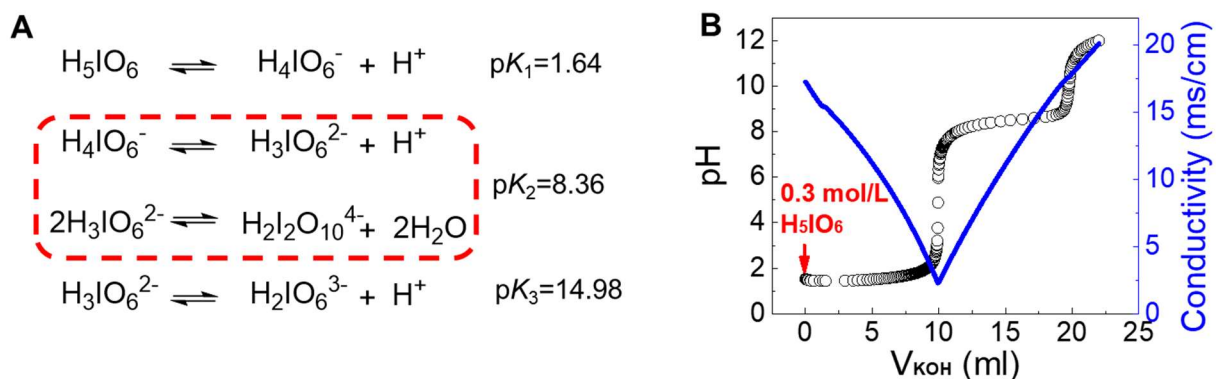**Figure S5.** Zeta potentials of PO-CNCs from 14 days reaction.

Figure S6. A) The deprotonation steps of periodic acid at diverse pH values. B) Conductivity and pH value during the titration process by adding aqueous KOH solution (0.2 g/mL).

The existing and the definition of inactive of $H_2I_2O_{10}^{4-}$ led to a conclusion that the equilibrium of $H_2I_2O_{10}^{4-}$ and $H_3IO_6^{2-}$ existed in the isolation process at pH 10. The main species for oxidation was $H_3IO_6^{2-}$ (Figure S6A).

From Figure S6B, there were three steps of deprotonation in the pH range of 1 to 12[11]. At pH 10, the form of periodate should be $H_2I_2O_{10}^{4-}$ and $H_3IO_6^{2-}$ because of the presence of the plateau stage at this pH during the addition of aqueous KOH solution. Furthermore, because the pH value of reaction solution remained at pH 10 and did not change at the end of the reaction, the reaction solution for isolation should only contain the same type of ions as during the reaction.
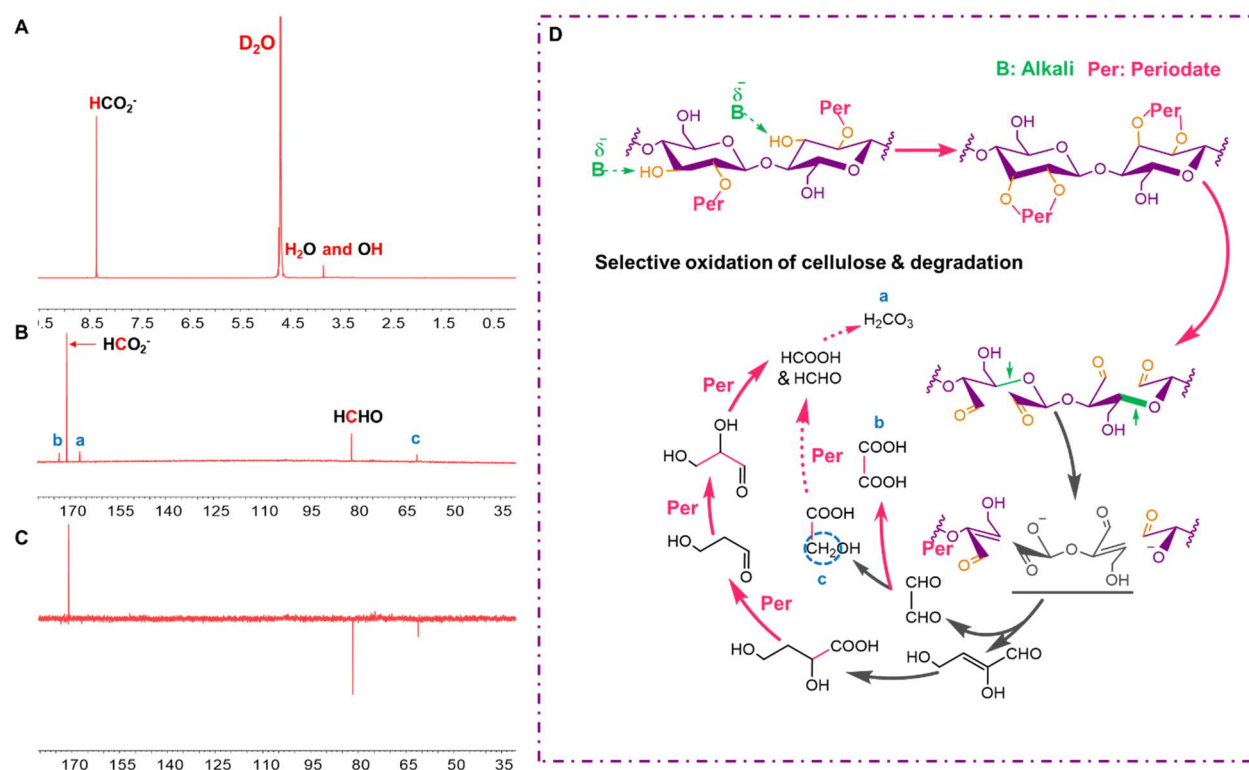
Figure S7. A), B) and C) are ^{1}H, ^{13}C NMR spectra and APT of soluble part from isolation process in D_2O. D) Proposed route for the selective oxidation of cellulose and further degradation.

According to the NMR spectrum, the main product was formic acid. For the peak a in ^{13}C NMR spectra, we proposed this is the carbon spectrum of bicarbonate, as to the peak b, we proposed this is the carbon spectrum of oxalic acid. For the peak c in Figure S7B, We proposed that this peak belongs to the -CH$_2$ group of glycolic acid.
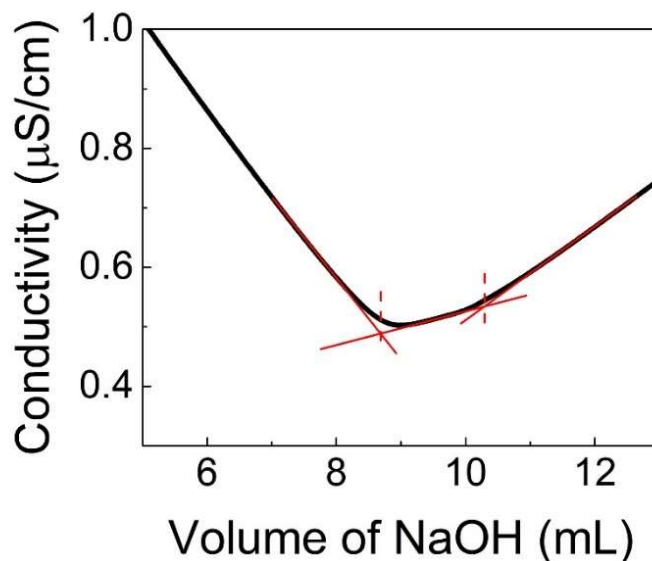
Figure S8. PO-CNCs from 14 days reaction in acidic solutions titrated with aqueous NaOH solution (0.05 M).

The amount of carboxyl groups on the PO-CNCs surface (14 days) was determined to be 0.45±0.07 mmol/g.

From the titration for determination of contents of aldehyde groups, 10 mL hydroxylamine hydrochloride solution (5% w/w) did not change the pH value obviously. From elemental analysis, we did not find detectable nitrogen in our samples. Thus, the aldehyde groups could not be found in produced PO-CNCs and total solid.

Table S2. Size distributions of PO-CNCs from reactions of various days.

Days	Size	
	Length (nm)	Diameter (nm)
1	118.4 ± 23.9	5.3 ± 2.4
3	116 ± 18.9	4.1 ± 2.0
6	118.2 ± 17.4	3.7 ± 1.9
10	117.8 ± 16.5	4.9 ± 2.1
14	120.1 ± 17.3	5 ± 2.5
30	119.5 ± 14.7	4.4 ± 1.9
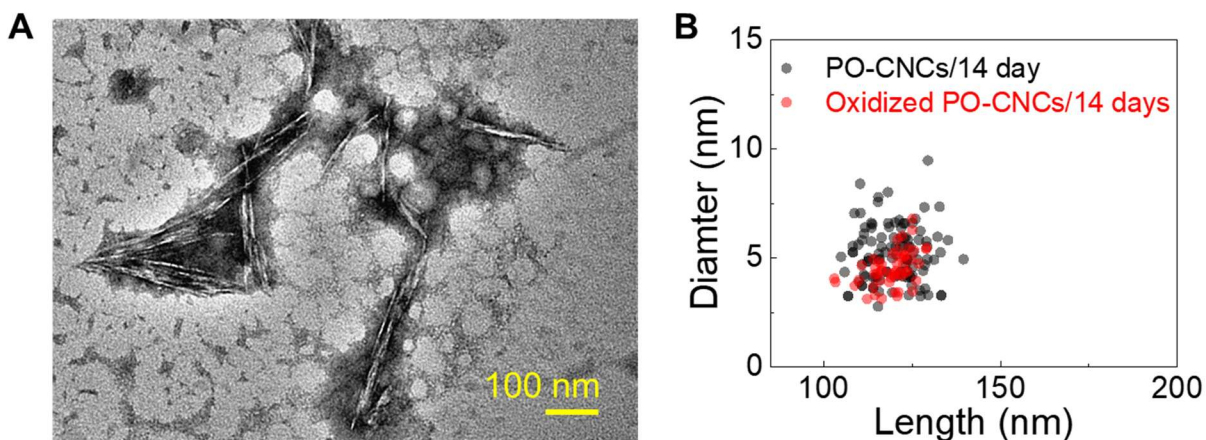
Figure S9. TEM image and size distribution of oxidized PO-CNCs

7.04 g of H_5IO_6 was added into the suspension with 1 g of PO-CNCs and the pH of this mixture was adjusted to 10 by aqueous KOH (4 mol/L), the total volume of reactions were fixed to 150 mL. The reactions were performed at room temperature (~25 °C) under continuous stirring without light for 14 days.

With same post-treatment as mentioned in Method, obtained oxidized PO-CNCs from 14 days reaction was purified before the analysis with TEM.

Oxidized PO-CNCs still has the morphology as the needle-like nanoparticles. The size distribution of oxidized PO-CNCs did not show obvious difference from the PO-CNCs: average diameter and length of 120.1±17.3 and 5±2.5 nm for PO-CNCs/14 days, while average diameter and length of 119.4±13.1 and 4.8±1.8 nm for oxidized PO-CNCs/14 days. Thus, the weight loss should be due to the oxidation and degradation of a small part of PO-CNCs.
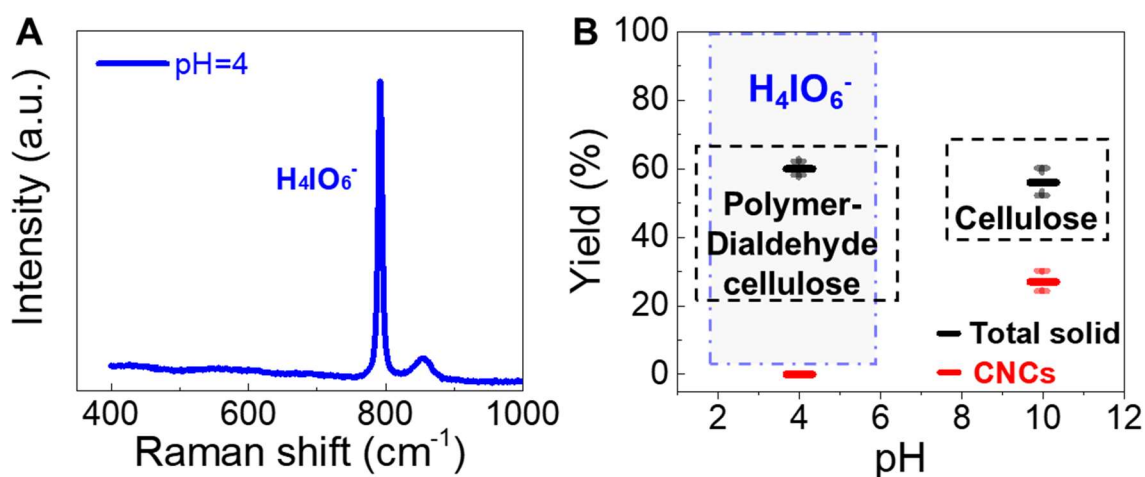
Figure S10 A) Representative Raman spectra for isolation solution at pH 4 without adding MCC. B) Isolation on MCC at pH of 10 and 4.

At pH value of 4, the form of periodate was $H_4IO_6^-$[11a].

Periodate oxidation with same equivalent of $NaIO_4$ resulted the polymeric dialdehyde cellulose (Figure S11) with 9.8 mmol/g of aldehyde groups after 3 days oxidation[12].

Figure S11. FTIR spectra of produced solid from periodate oxidation at pH 4
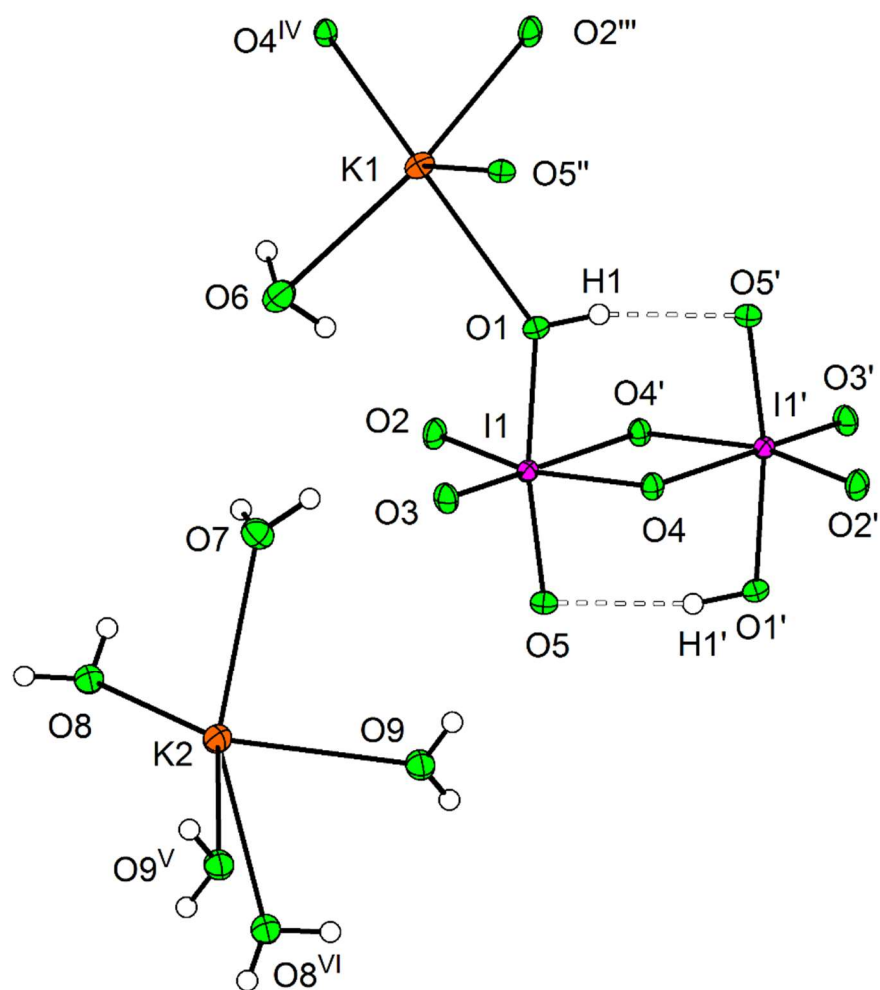
Figure S12. Molecular structure of $K_4H_2I_2O_{10} \cdot 8H_2O$. The structure was reported previously, with slightly different cell parameters[6].

Table S3. Crystal data and structure refinement for $K_4H_2I_2O_{10} \cdot 8H_2O$.

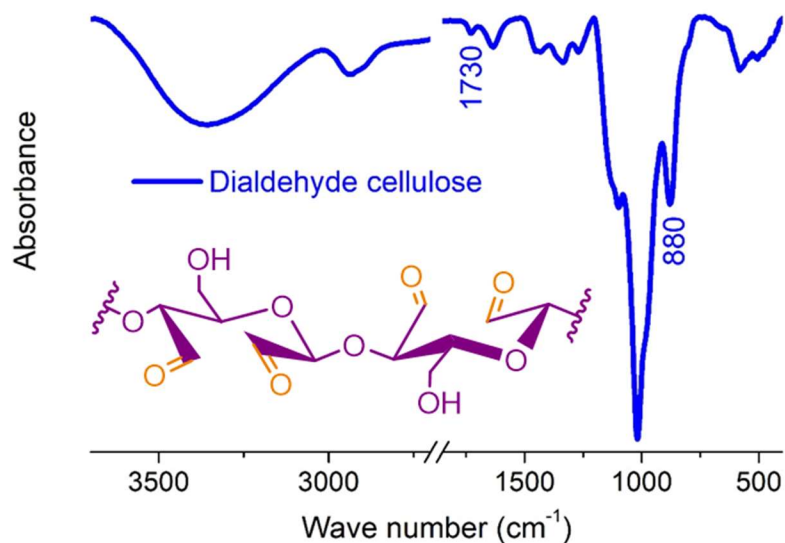|	
Empirical formula	H18 I2 K4 O18
Formula weight	716.34
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 7.0466(6) Å α= 90.187(7)°.
	b = 7.1163(6) Å β= 98.163(7)°.
	c = 10.4929(9) Å γ= 116.047(6)°.
Volume	466.67(7) Å^3
Z	1
Density (calculated)	2.549 Mg/m^3
Absorption coefficient	4.341 mm^{-1}
F(000)	344
Crystal size	0.500 x 0.400 x 0.340 mm^3
Theta range for data collection	1.966 to 26.698°.
Index ranges	-8<=h<=8, -8<=k<=8, -13<=l<=13
Reflections collected	6220
Independent reflections	1946 [R(int) = 0.0236]
Completeness to theta = 25.242°	99.3 %
Absorption correction	Numerical
Max. and min. transmission	0.4831 and 0.2049
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1946 / 0 / 146
Goodness-of-fit on F^2	1.283
Final R indices [I>2sigma(I)]	R1 = 0.0164, wR2 = 0.0436
R indices (all data)	R1 = 0.0165, wR2 = 0.0436
Extinction coefficient	0.0557(16)
Largest diff. peak and hole	0.779 and -0.506 e.Å^{-3}

Table S4. Bond lengths [Å] and angles [°] for $K_4H_2I_2O_{10} \cdot 8H_2O$.

_____

I(1)-O(3)	1.8094(18)
I(1)-O(2)	1.8120(17)
I(1)-O(5)	1.8282(18)
I(1)-O(1)	1.9576(18)
I(1)-O(4)	1.9786(17)
I(1)-O(4)#1	1.9980(17)
I(1)-I(1)#1	3.1094(4)
I(1)-K(1)#2	3.7018(7)
I(1)-K(1)#3	3.7047(6)
K(1)-O(1)	2.6656(19)
K(1)-O(4)#4	2.7063(19)
K(1)-O(6)	2.830(2)
K(1)-O(2)#2	2.8305(19)
K(1)-O(5)#5	2.854(2)
K(1)-O(2)#5	2.9182(19)
K(1)-O(7)#5	3.012(2)
K(1)-O(9)#5	3.013(2)
K(1)-K(2)#5	3.9532(8)
K(1)-K(1)#6	4.0532(11)
K(2)-O(9)	2.741(2)
K(2)-O(8)	2.752(2)
K(2)-O(7)	2.761(2)
K(2)-O(8)#7	2.764(2)
K(2)-O(9)#8	2.843(2)
K(2)-O(7)#9	2.887(2)
K(2)-O(6)#3	3.014(2)
K(2)-O(6)#9	3.065(2)
K(2)-K(2)#7	3.6571(11)
K(2)-K(2)#8	4.4269(12)
K(2)-K(2)#9	4.4302(12)
O(3)-I(1)-O(2)	101.53(8)
O(3)-I(1)-O(5)	97.03(8)
O(2)-I(1)-O(5)	96.99(8)
O(3)-I(1)-O(1)	89.87(8)

O(2)-I(1)-O(1)	88.74(8)
O(5)-I(1)-O(1)	169.95(8)
O(3)-I(1)-O(4)	91.50(8)
O(2)-I(1)-O(4)	164.94(8)
O(5)-I(1)-O(4)	88.78(8)
O(1)-I(1)-O(4)	83.72(8)
O(3)-I(1)-O(4)#1	167.63(8)
O(2)-I(1)-O(4)#1	89.18(8)
O(5)-I(1)-O(4)#1	87.67(8)
O(1)-I(1)-O(4)#1	84.15(8)
O(4)-I(1)-O(4)#1	77.13(8)
O(3)-I(1)-I(1)#1	130.11(6)
O(2)-I(1)-I(1)#1	127.24(6)
O(5)-I(1)-I(1)#1	87.73(6)
O(1)-I(1)-I(1)#1	82.23(6)
O(4)-I(1)-I(1)#1	38.78(5)
O(4)#1-I(1)-I(1)#1	38.34(5)
O(3)-I(1)-K(1)#2	141.11(6)
O(2)-I(1)-K(1)#2	48.01(6)
O(5)-I(1)-K(1)#2	108.80(6)
O(1)-I(1)-K(1)#2	69.15(6)
O(4)-I(1)-K(1)#2	116.94(5)
O(4)#1-I(1)-K(1)#2	45.48(5)
I(1)#1-I(1)-K(1)#2	80.666(12)
O(3)-I(1)-K(1)#3	116.96(6)
O(2)-I(1)-K(1)#3	50.76(6)
O(5)-I(1)-K(1)#3	48.79(6)
O(1)-I(1)-K(1)#3	133.40(6)
O(4)-I(1)-K(1)#3	128.95(5)
O(4)#1-I(1)-K(1)#3	74.63(5)
I(1)#1-I(1)-K(1)#3	103.282(12)
K(1)#2-I(1)-K(1)#3	66.358(16)
O(1)-K(1)-O(4)#4	130.30(6)
O(1)-K(1)-O(6)	78.42(6)
O(4)#4-K(1)-O(6)	78.85(6)
O(1)-K(1)-O(2)#2	94.65(6)

O(4)#4-K(1)-O(2)#2	57.80(5)
O(6)-K(1)-O(2)#2	115.57(6)
O(1)-K(1)-O(5)#5	87.12(6)
O(4)#4-K(1)-O(5)#5	139.44(6)
O(6)-K(1)-O(5)#5	131.02(6)
O(2)#2-K(1)-O(5)#5	112.04(5)
O(1)-K(1)-O(2)#5	141.95(6)
O(4)#4-K(1)-O(2)#5	83.48(5)
O(6)-K(1)-O(2)#5	132.20(6)
O(2)#2-K(1)-O(2)#5	90.35(5)
O(5)#5-K(1)-O(2)#5	56.36(5)
O(1)-K(1)-O(7)#5	143.22(6)
O(4)#4-K(1)-O(7)#5	69.26(6)
O(6)-K(1)-O(7)#5	76.01(6)
O(2)#2-K(1)-O(7)#5	120.13(6)
O(5)#5-K(1)-O(7)#5	90.07(6)
O(2)#5-K(1)-O(7)#5	56.19(5)
O(1)-K(1)-O(9)#5	69.68(6)
O(4)#4-K(1)-O(9)#5	142.42(6)
O(6)-K(1)-O(9)#5	75.07(6)
O(2)#2-K(1)-O(9)#5	159.64(6)
O(5)#5-K(1)-O(9)#5	56.07(6)
O(2)#5-K(1)-O(9)#5	94.40(6)
O(7)#5-K(1)-O(9)#5	78.44(6)
O(1)-K(1)-I(1)#2	106.68(5)
O(4)#4-K(1)-I(1)#2	31.76(4)
O(6)-K(1)-I(1)#2	92.29(5)
O(2)#2-K(1)-I(1)#2	28.41(4)
O(5)#5-K(1)-I(1)#2	136.64(4)
O(2)#5-K(1)-I(1)#2	95.38(4)
O(7)#5-K(1)-I(1)#2	100.36(4)
O(9)#5-K(1)-I(1)#2	167.25(4)
O(1)-K(1)-I(1)#5	113.30(5)
O(4)#4-K(1)-I(1)#5	110.67(4)
O(6)-K(1)-I(1)#5	144.99(5)
O(2)#2-K(1)-I(1)#5	96.87(4)

O(5)#5-K(1)-I(1)#5	28.82(4)
O(2)#5-K(1)-I(1)#5	28.75(3)
O(7)#5-K(1)-I(1)#5	76.44(4)
O(9)#5-K(1)-I(1)#5	78.59(4)
I(1)#2-K(1)-I(1)#5	113.643(15)
O(1)-K(1)-K(2)#5	99.06(5)
O(4)#4-K(1)-K(2)#5	98.63(4)
O(6)-K(1)-K(2)#5	49.42(4)
O(2)#2-K(1)-K(2)#5	156.08(4)
O(5)#5-K(1)-K(2)#5	88.25(4)
O(2)#5-K(1)-K(2)#5	90.81(4)
O(7)#5-K(1)-K(2)#5	44.18(4)
O(9)#5-K(1)-K(2)#5	43.80(4)
I(1)#2-K(1)-K(2)#5	127.803(18)
I(1)#5-K(1)-K(2)#5	95.573(16)
O(1)-K(1)-K(1)#6	128.58(5)
O(4)#4-K(1)-K(1)#6	63.00(4)
O(6)-K(1)-K(1)#6	141.72(5)
O(2)#2-K(1)-K(1)#6	46.05(4)
O(5)#5-K(1)-K(1)#6	82.14(4)
O(2)#5-K(1)-K(1)#6	44.29(4)
O(7)#5-K(1)-K(1)#6	87.13(4)
O(9)#5-K(1)-K(1)#6	135.23(5)
I(1)#2-K(1)-K(1)#6	56.856(15)
I(1)#5-K(1)-K(1)#6	56.787(14)
K(2)#5-K(1)-K(1)#6	130.43(2)
O(9)-K(2)-O(8)	141.90(7)
O(9)-K(2)-O(7)	87.64(7)
O(8)-K(2)-O(7)	76.40(7)
O(9)-K(2)-O(8)#7	75.37(7)
O(8)-K(2)-O(8)#7	96.94(6)
O(7)-K(2)-O(8)#7	143.00(7)
O(9)-K(2)-O(9)#8	75.11(7)
O(8)-K(2)-O(9)#8	140.58(6)
O(7)-K(2)-O(9)#8	130.13(7)
O(8)#7-K(2)-O(9)#8	77.31(7)

O(9)-K(2)-O(7)#9	130.73(7)
O(8)-K(2)-O(7)#9	79.28(6)
O(7)-K(2)-O(7)#9	76.69(6)
O(8)#7-K(2)-O(7)#9	138.65(6)
O(9)#8-K(2)-O(7)#9	80.23(6)
O(9)-K(2)-O(6)#3	76.33(6)
O(8)-K(2)-O(6)#3	66.51(6)
O(7)-K(2)-O(6)#3	76.99(6)
O(8)#7-K(2)-O(6)#3	67.23(6)
O(9)#8-K(2)-O(6)#3	138.88(6)
O(7)#9-K(2)-O(6)#3	140.72(6)
O(9)-K(2)-O(6)#9	135.33(6)
O(8)-K(2)-O(6)#9	66.61(6)
O(7)-K(2)-O(6)#9	136.91(6)
O(8)#7-K(2)-O(6)#9	65.64(6)
O(9)#8-K(2)-O(6)#9	75.82(6)
O(7)#9-K(2)-O(6)#9	75.46(6)
O(6)#3-K(2)-O(6)#9	106.04(5)
O(9)-K(2)-K(2)#7	113.66(5)
O(8)-K(2)-K(2)#7	48.61(5)
O(7)-K(2)-K(2)#7	115.26(5)
O(8)#7-K(2)-K(2)#7	48.34(5)
O(9)#8-K(2)-K(2)#7	114.54(5)
O(7)#9-K(2)-K(2)#7	115.30(5)
O(6)#3-K(2)-K(2)#7	53.67(4)
O(6)#9-K(2)-K(2)#7	52.37(4)
O(9)-K(2)-K(1)#3	49.54(4)
O(8)-K(2)-K(1)#3	95.81(5)
O(7)-K(2)-K(1)#3	49.50(4)
O(8)#7-K(2)-K(1)#3	96.30(5)
O(9)#8-K(2)-K(1)#3	123.48(4)
O(7)#9-K(2)-K(1)#3	125.03(4)
O(6)#3-K(2)-K(1)#3	45.49(4)
O(6)#9-K(2)-K(1)#3	151.53(4)
K(2)#7-K(2)-K(1)#3	99.16(2)
O(9)-K(2)-K(2)#8	38.36(4)

O(8)-K(2)-K(2)#8	169.49(5)
O(7)-K(2)-K(2)#8	112.85(5)
O(8)#7-K(2)-K(2)#8	72.70(5)
O(9)#8-K(2)-K(2)#8	36.75(4)
O(7)#9-K(2)-K(2)#8	107.15(5)
O(6)#3-K(2)-K(2)#8	109.72(5)
O(6)#9-K(2)-K(2)#8	106.44(5)
K(2)#7-K(2)-K(2)#8	121.01(3)
K(1)#3-K(2)-K(2)#8	87.27(2)
O(9)-K(2)-K(2)#9	113.55(5)
O(8)-K(2)-K(2)#9	74.48(5)
O(7)-K(2)-K(2)#9	39.36(4)
O(8)#7-K(2)-K(2)#9	170.71(5)
O(9)#8-K(2)-K(2)#9	106.92(5)
O(7)#9-K(2)-K(2)#9	37.33(4)
O(6)#3-K(2)-K(2)#9	111.36(5)
O(6)#9-K(2)-K(2)#9	106.94(4)
K(2)#7-K(2)-K(2)#9	122.98(3)
K(1)#3-K(2)-K(2)#9	88.24(2)
K(2)#8-K(2)-K(2)#9	115.74(2)
I(1)-O(1)-K(1)	141.80(9)
I(1)-O(2)-K(1)#2	103.58(7)
I(1)-O(2)-K(1)#3	100.49(7)
K(1)#2-O(2)-K(1)#3	89.66(5)
I(1)-O(4)-I(1)#1	102.88(8)
I(1)-O(4)-K(1)#10	141.65(8)
I(1)#1-O(4)-K(1)#10	102.75(7)
I(1)-O(5)-K(1)#3	102.39(8)
K(1)-O(6)-K(2)#5	85.08(6)
K(1)-O(6)-K(2)#9	159.04(8)
K(2)#5-O(6)-K(2)#9	73.96(5)
K(2)-O(7)-K(2)#9	103.31(6)
K(2)-O(7)-K(1)#3	86.33(6)
K(2)#9-O(7)-K(1)#3	164.65(8)
K(2)-O(8)-K(2)#7	83.06(6)
K(2)-O(9)-K(2)#8	104.89(7)

K(2)-O(9)-K(1)#3   86.66(6)

K(2)#8-O(9)-K(1)#3   163.26(8)

_____

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+2   #2 -x+1,-y+2,-z+2   #3 x,y-1,z

#4 x+1,y+1,z   #5 x,y+1,z   #6 -x+1,-y+3,-z+2

#7 -x+1,-y,-z+1   #8 -x,-y,-z+1   #9 -x+1,-y+1,-z+1
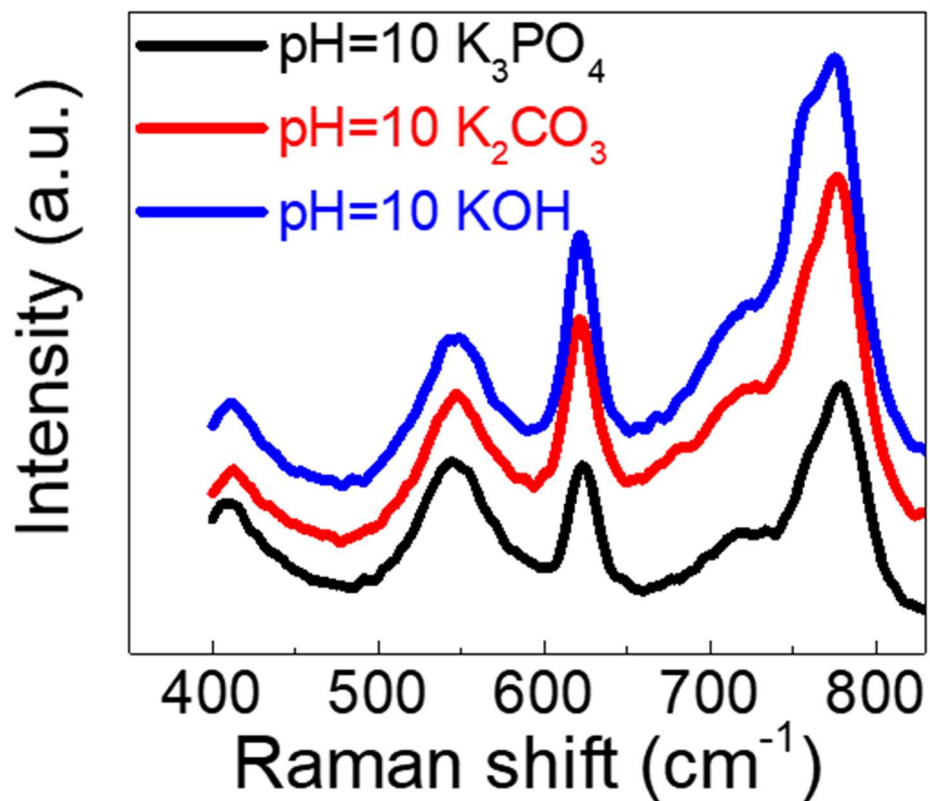
#10 x-1,y-1,z

Figure S13. Representative Raman spectra of isolation solutions at pH 10 which was adjusted with a variety of different bases.

In these three solutions, dimeric orthoperiodate (in the form of $H_2I_2O_{10}^{4-}$) should be present according to their Raman spectra[11b, 13].

Moreover, it is known that HCO_3^- and HPO_4^{2-} are the predominant ions of their species in each solution at pH 10[14].

Table S5. The chemical compositions of various lignocelluloses.

Sample	$TG_{no\ extracted}$ [%]	Extract portion [%]	Lignin content [%]	Cellulose content [%]	Holocellulose-content [%]	Hemicellulose-content [%]	Ash content [%]
Pulp	99.3	-	-	95.6	-	-	-
Flax	94.24	1.75	7.07	68	84.79	16.79	1.69
Kenaf	92.52	0.73	13.27	59.75	87.13	27.38	1.19
Scots Pine	92.21	2.12	26.55	48.14	74.82	26.68	0.24
Eurobean beech	91.94	1.46	24.29	39.68	75.35	35.67	0.34

For all analyzes, small amounts of residues of secondary components always remain in the samples despite the most careful work. Therefore, results of >100% of all individual components are resulted.

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