Supporting Information

High-Yielding One-Pot Synthesis of Glucose from Cellulose Using Simple Activated Carbons and Trace Hydrochloric Acid

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Figures:

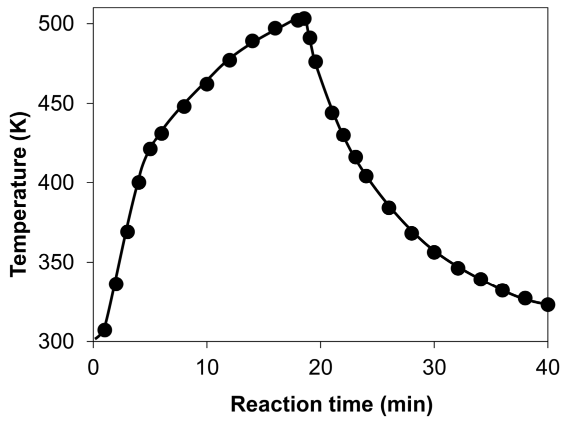

Figure S1. Temperature profile of the rapid heating-cooling conditions.

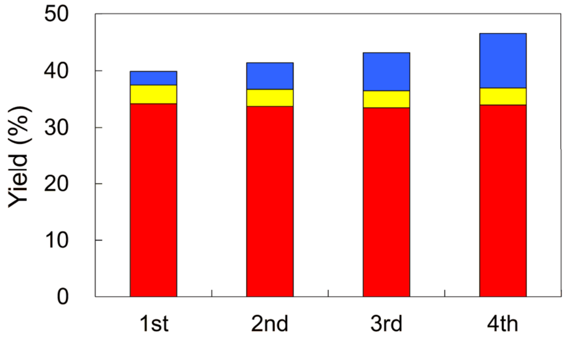

Figure S2. Reuse tests of K26 for hydrolysis of ball-milled cellulose under rapid heating-cooling conditions at 503 K. Bottom (red): glucose; middle (yellow): fructose and mannose; top (cyan): oligomers.

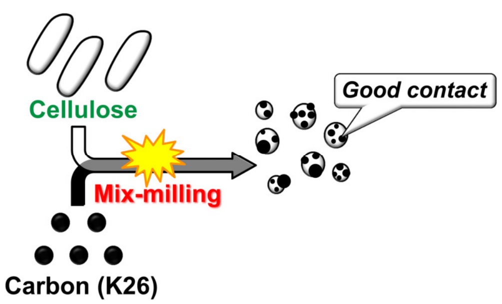

Figure S3. Schematic representation of mix-milling.

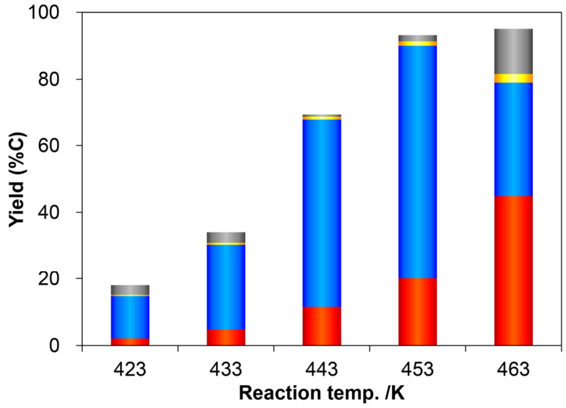

Figure S4. Temperature effect on the hydrolysis of mix-milled cellulose in water. Reaction time 20 min. Red: glucose; blue: oligomers; yellow: fructose and mannose; gray: others.

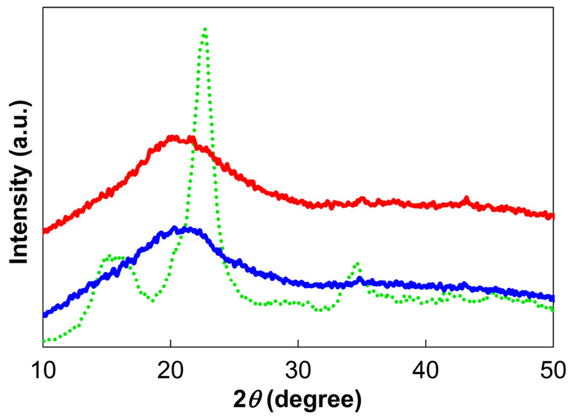

Figure S5. XRD patterns of the mix-milled K26 and cellulose (red solid line), singularly ball-milled cellulose (blue solid line), and microcrystalline cellulose (green dashed line).

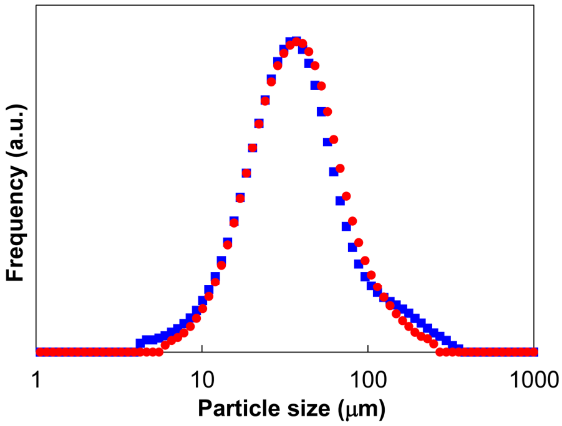

Figure S6. Distributions of particle diameters of the mix-milled K26 and cellulose (red circle ●) and simple mixture of ball-milled cellulose and ball-milled K26 (blue cubic ■).

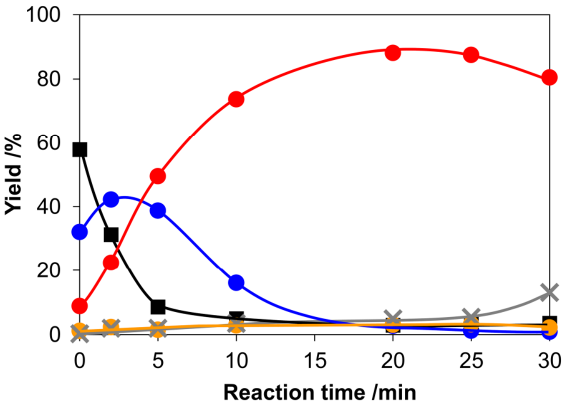

Figure S7. Time course of the hydrolysis of mix-milled cellulose in 0.012% HCl aq. at 453 K. Black square (■): remaining cellulose; red circle (●): glucose; blue circle (●): oligomers; yellow circle (●): fructose and mannose; gray cross (×): others.

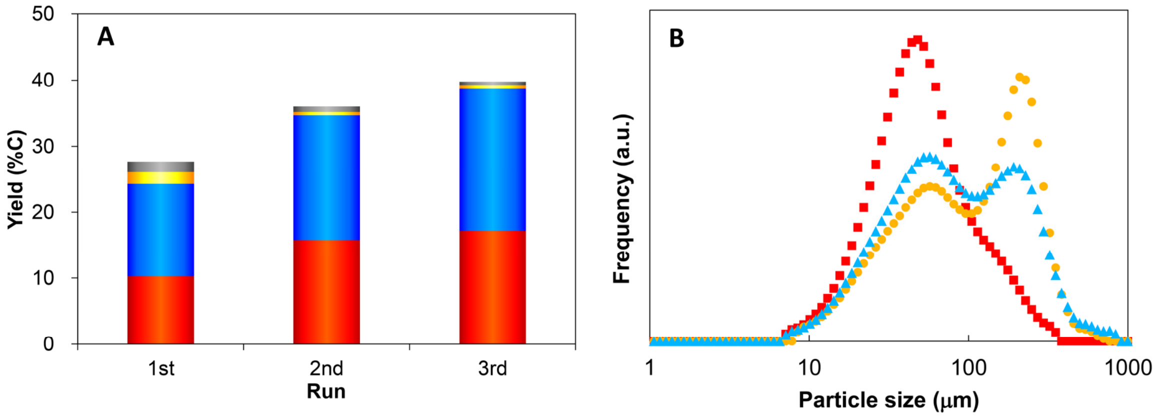

Figure S8. Reuse experiments of mix-milled K26. (A) Reaction results. Red: glucose; blue: oligomers; yellow: fructose and mannose; gray: others. (B) Particle size distributions. Red square (■): first run; yellow circle (●): second run; cyan triangle (▲): third run.

Reaction conditions: cellulose 200 g L^{-1}, K26 31 g L^{-1}, solvent 0.012% HCl aq., T = 453 K, 0 min (rapid heating and cooling). The additive amount of fresh cellulose was just equivalent to that consumed in the previous run, keeping a constant amount of cellulose in each run.

The slight increases in yields of products are reasonable as the residual solid cellulose has undergone hydrolysis to decrease the degree of polymerization in the previous run. This remaining part should be relatively easily converted to soluble products in the subsequent run.

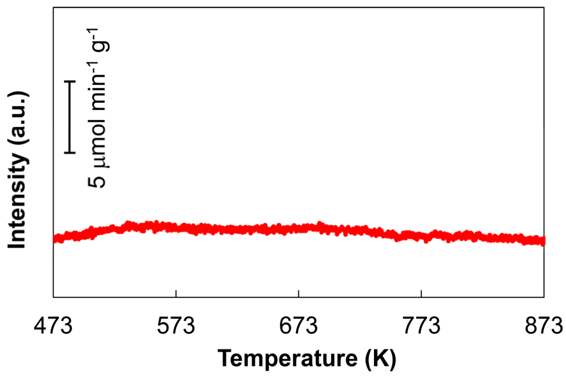

Figure S9. NH_3-TPD measurement of K26. Rate of temperature increase 10 K min^{-1}.

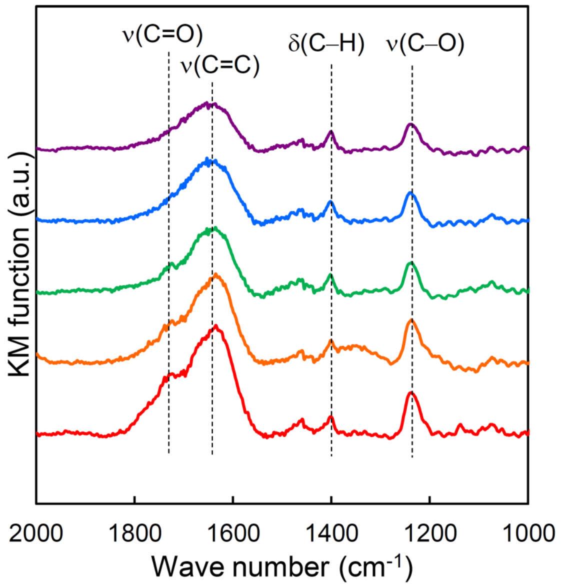

Figure S10. DRIFT spectra of heat-treated K26s. Red: non-treated; orange: pre-treated at 673 K; green: 873 K; cyan: 1073 K; purple: 1273 K.

A peak at 1740 cm^{-1} ascribed to C=O stretching decreased with elevating the pretreatment temperature (non-treated to treated at 1073 K), corresponding to the reduction of carboxylic acids and lactones as indicated by the Boehm titration.[1] The C–O stretching peak at 1240 cm^{-1} gradually decreased but still remained at 1273 K, due to the presences of ether groups[2] and a small amount of phenolic groups. A peak for aromatic rings (C=C) at 1640 cm^{-1} also diminished, which might be due to the reduction of change of dipole moment in the vibration by the removal of oxygenated groups.

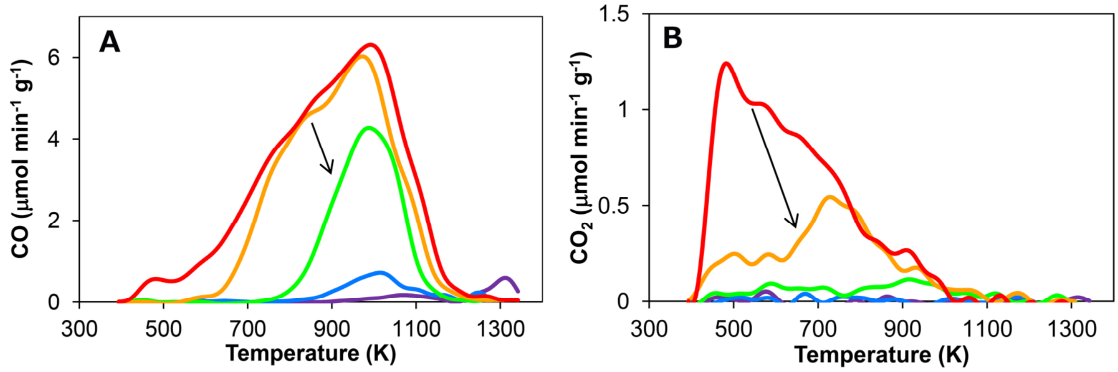

Figure S11. TPD measurement of heat-treated K26s. Rate of temperature increase 2 K min^{-1}. (**A**) CO, m/z = 28. (**B**) CO_2, m/z = 44. Red: non-treated; orange: pre-treated at 673 K; green: 873 K; cyan: 1073 K; purple: 1273 K.

The peaks were assigned according to the literature.[2] CO: lactone and anhydride (600-1000 K), phenol (700-1100 K), ether and carbonyl (1000-1300 K). CO_2: carboxylic acid (400-600 K), lactone and anhydride (600-1000 K).

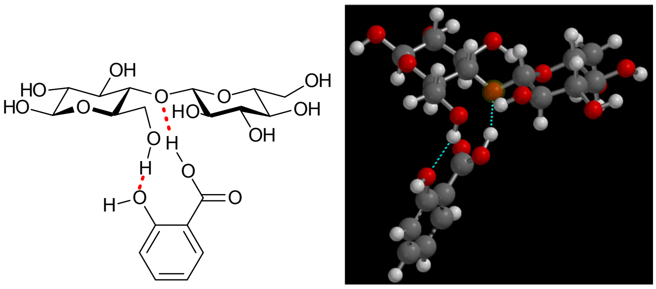

Figure S12. Proposed interaction between β-glucans and salicylic acid, predicted by Spartan'08.

Tables:

Table S1. Production of high concentration of glucose[a]

Entry	Concentration of ball-milled cellulose (g L-water^{-1})	Concentration of K26 (g L-water^{-1})	S/C	Conv. (%)	Yield of glucose (%)	Concentration of glucose (%)
S1	8.1	1.3	6.5	60	36	0.32
S2	150	13	12	57	38	6.0
S3	300	25	12	58	40	12

[a]Reaction conditions: water 40 mL. Rapid heating-cooling conditions (Figure S1).

Table S2. Effect of concentration of cellulose on the hydrolysis by K26[a]

Entry	Concentration of ball-milled cellulose (g L-water^{-1})	S/C	Conversion rate of cellulose[b] (g L-water^{-1} h^{-1})	Yield of glucose (%)
S4	8.1	6.5	8.7	40
S5	16	13	16	40
S6	24	19	24	39
S7	40	32	35	38

[a]Reaction conditions: K26 50 mg (1.25 g L-water^{-1}), water 40 mL. Rapid heating-cooling conditions (Figure S1), but the top temperature was 508 K. [b]Based on the total reaction time (40 min).

Table S3. Effect of salts on the hydrolysis of cellulose[a]

Entry	Salt	Conv. (%)	Yield based on carbon (%)							
			Sugar product					By-product		
			Glucose	Fructose	Mannose	Oligomers	Total	Levoglucosan	5-HMF[b]	Others[c]
1	None	28	4.6	0.5	0.6	15	21	0.2	1.8	5
S8	3.2 mM NaCl	15	1.7	0.4	0.7	5.6	8.4	0.1	1.0	6
S9	1.6 mM Na_2SO_4	7	0.3	0.1	0.1	2.3	2.8	0.4	0.2	4

[a]Conditions: cellulose 324 mg, distilled water 40 mL, rapid heating-cooling conditions (503 K; Figure S1). [b]5-Hydroxymethylfurfural. [c](conversion) – (total yield of the shown products).

References:

(1) Fanning, P. E.; Vannice, M. A. *Carbon* **1993**, *31*, 721-730.

(2) Figueiredo, J. L.; Pereira, M. F. R.; Freitas, M. M. A.; Órfão, J. J. M. *Carbon* **1999**, *37*, 1379-1389.