Supplementary information for:

Highly efficient mechano-catalytic depolymerization of cellulose by formation of branched glucan chains

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Experimental section

Materials

Microcrystalline cellulose (Avicel, 4 % moisture, DP 215), sulfanilic acid (98%), sodium nitrite (98%), hyphophorous acid (H_3PO_2) (50% in water), tetraethylorthosilicate (TEOS, 98%) and furfural alcohol (98%) were purchased from Alfa Aesar. Sulfuric acid (H_2SO_4, both 98% and 0.005 M), 200 proof ethanol, N,N-dimethylformamide (DMF) (99.8%), methanol (99.8%), acetone (99.8%) and 12.1 M hydrochloric acid (HCl) were purchased from Fisher Scientific. Linear glucan β(1→4) oligomers (cellotriose (95%), cellotetraose (95%), cellopentaose (95%) and cellohexaose (94%)) were purchased from Megazyme. Oxalic acid (99%), L-lysine (98%), levoglucosan (99%), 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS, 97%) cellobiose (99%), maltose monohydrate (99%), isomaltose (98%), glucose (99%) and deuterium oxide (D_2O, 99.9%) were purchased from Sigma Aldrich.

Preparation of acidulated ball-milled cellulose

For the impregnation process, microcrystalline cellulose was first impregnated with 0.25 mmol H_2SO_4 g^{-1} and LMSs with a LMS:MCC weight ratio of 12.5:87.5 with a total of 10 g of saccharide. Typically, 1.25 g of LMS and 140 μL of 98% H_2SO_4 were dissolved in 20 mL of water, and then added to 8.75 g of MCC drop-wisely. In the case of *i*h-N-ABMC sample, only H_2SO_4 was impregnated with 10 g of MCC. After the impregnation, the samples were left in an oven at 50 °C for 2.0 days to remove the water and form acidulated microcrystalline cellulose with co-impregnated LMS. For the ball-milling process, 2.0 g of the acidulated microcrystalline cellulose samples with different LMSs were ball-milled for up to 6.0 h using an SFM-3 high-speed shimmy ball-mill (MTI Corporation). Milling proceeded in 30 minute durations

with 15 minute cool down periods to avoid heating above 50 °C. After milling the samples were stored at -18 °C. A control sample was also prepared by physically mixing glucose with the microcrystalline cellulose only impregnated with acid. The sample is named 0h-PM-ABMC. Typically, 0.25 g of D-glucose powder was added to 1.75 g of MCC and mixed with a spatula inside the milling canister followed by the standard milling procedure.

Characterization of acidulated ball-milled cellulose

The amount of soluble material in each sample was determined by dispersing 40 mg of *i*h-*j*-ABMC in 0.80 mL of deionized water by 15 minutes of sonication and 3 minutes of vortexing followed by filtration using a 0.20 μm pore-size filter and analyzed using a high performance liquid chromatography (HPLC) (LC-20AT, Shimadzu) equipped with refractive index (RID-10A) and UV–Vis (SPD-2AV) detectors at oven temperature of 85 °C. An Agilent Hi-Plex-Na HPLC column (7.7 mm (ID), 300 mm (Length), 10 μm (particle size)) with a guard column was used. HPLC grade water (Fisher) was used as a mobile phase with a flow rate of 0.3 mL minute^{-1}.

^{1}H-NMR was performed on a Bruker Advance 400 (400 MHz) spectrometer to determine the prevalence of glycosidic linkages and reducing ends. Samples were prepared by dispersing 5.0 wt.% *i*h-*j*-ABMC in D_2O with 10 mM 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) as an internal standard. ^{1}H-NMR samples were sonicated for 15 minutes and votexed for 3 minutes followed by filtration before the measurement. The ^{1}H-NMR was performed with 32 scans.

Determination of levoglucosan was performed using gas chromatography/mass spectroscopy (GC/MS) using an Agilent 7890A gas chromatagraph (GC) with flame ionization detector (FID), an Agilent DB-5 column (30 m length, 0.320 mm diameter, 1.5 μm film) and Agilent 5975C mass spectrometer (MS). The GC oven was heated from -30 to 260 °C over 71 minutes.

Catalyst synthesis

3DOm carbon with 35 nm cage size was prepared according to literature.[1] Briefly, 35 nm silica nanoparticles (SNPs) were prepared by mixing 0.198 L-lysine, 13.3 g TEOS and 180 mL of water at 90 °C in a Teflon bottle stirring at 1000 rpm. An additional amount of 26.6 g of TEOS was added after 24 h and

48 h for a total of 66.5 g TEOS. The solution was stirred for an additional 24 h after the adding the last amount of TEOS. The resulting solution was evaporated in a convection oven at 70 °C for 72 h. The precipitated SNPs were calcined for 24 h at 600 °C (with 3 °C min^{-1} heating) to remove L-lysine. To prepare the resin, 0.10 g oxalic acid were dissolved in 20 g of furfural alcohol. The SNPs were impregnated with the furfural alcohol solution by incipient wetness. Excess furfuryl alcohol solution was removed by whipping with filter paper. The sample was then put in a 70 °C oven for 48 h and subsequently carbonized under nitrogen at 200 °C for 3 h followed by 900 °C for 2 h (1 °C min^{-1} heating). The sample was then treated twice under hydrothermal conditions at 150 °C with 6 M KOH for 2 days to remove silica. Finally, the carbon was washed in 1 L of 70 °C water for 3 h repeatedly until the pH of the solution fell below 8. The resulting 3DOm carbon was dried overnight at 70 °C.

The surface functionalization of amorphous carbon by benzenesulfonic acid radicals derived from diazonium salts has been reported previously.[2] 60 mL deionized water were mixed with 4 mL of 12.1 M HCl and 0.6 g of sulfanilic acid. This solution immersed in an ice bath and stirred for 5 minutes. 0.704 g of sodium nitrite were added to the solution and stirred for 10 minutes. A clear solution typically formed after 1 minute. At high concentrations of sodium nitrite and sulfanilic acid a white precipitate (likely the diazonium intermediate) formed after 5-7 minutes. 0.4 g of 3DOm carbon, 60 mL ethanol and 60 mL of 50% H_3PO_2 were added to the solution and stirred for 30 minutes, followed by the addition of 60 mL more H_3PO_2. The resulting solution was mixed for 8 h at ice bath temperature. After functionalization the catalyst was washed by shaking/sonicating 100 ml water, DMF, methanol and acetone, followed by washing with 2.0 L of 70 °C water. The sample was then washed overnight in 1 L of 70 °C water, filtered, then dried overnight at 70 °C. The number of acid sites was controlled by the amount of sulfanilic acid and sodium nitrite formed. It should be noted that the diazoniumsulfonated intermediate will precipitate after 10 minutes at 5 °C in water. Diazoniumsulfonate is not stable when dry and can spontaneously release nitrogen gas. Caution should be taken during filtration. Excess diazoniumsulfonated precipitate can be easily dissolved in DMF for safe separation and storage.

Characterization

The number of acid site and surface area were also measured for the carbon materials. Acid site concentration was measured by ion exchange with 0.050 M NaCl. Typically, 0.020 g of catalyst was placed in 10 mL of NaCl solution and sonicated for three hours. The solution was titrated with 0.010 M HCl with phenolphthalein as the indicator.[3] The carbon catalyst synthesized in this manor contained 0.57 mmol SO_3H g^{-1}. N_2 adsorption/desorption isotherms for different carbons were measured on an Autosorb®-iQ system (Quantachrome) at 77 K. Total surface area was calculated using the Brunauer–Emmett–Teller (BET) method.

LGA was confirmed by three techniques: HPLC (Fig. S1), ^{1}H-NMR (Fig. S2) and GC-MS (Fig. S3). A standard of LGA has identical retention time to the suspected peak observed in the HPLC at 42.5 minutes for the *i*h-*j*-ABMC samples on HPLC as shown in Fig. S1. The amount of LGA in each sample is shown in Table 2. ^{1}H-NMR results are shown in Fig. 2 for 2h-N-ABMC and 2h-G-ABMC show a singlet at 5.439 and a doublet at 4.082 (J = 7.8 Hz). The ^{1}H-NMR LGA standard shown in Fig. S2 confirms that these peaks are from LGA. Fig. S3 shows the mass spectra of LGA extracted from 2h-G-ABMC using a sample prepared by HPLC fraction collection of the peak suspected to be LGA and a standard LGA sample. The two spectra are nearly identical, with strong peaks at 60 and 73 m z^{-1}. Additionally, both spectra generated positive identification as LGA when searching the NIST spectral library. The search generated an R-match (software matching criteria; max score is 999) for LGA of 876 using the mass spectra obtained from the extracted LGA sample, while the pure LGA standard generated an R-match of 908 for LGA. This data indicates that the unknown sample extracted from 2h-G-ABMC on HPLC fraction collection is indeed LGA.

The hydrolysis reactions were performed using 1 wt.% 2h-G-ABMC obtained by ball-milling microcrystalline cellulose co-impregnated with glucose and acid for 2.0 h. 30 mg of 2h-G-ABMC were mixed with 20 mg of catalyst and 3 mL of deionized water, and sealed in a 5.0 mL borosilicate microwave heating vial (Chemglass). The reaction was performed on a Dynabloc aluminum stir plate with 22 (ID) × 35.6 (depth) mm holes (Ace Glass) at 120 °C for 2.0 h and at 165 °C from 10 to 60 minutes. Blank (no

additional acid) reactions and reactions with HCl (4.6 mM HCl) were run as control experiments at with 2h-G-ABMC at 120 °C. The turnover frequency (TOF) was determined by subtracting the moles of glucose produced during the blank reaction after 2.0 h from the moles of glucose produced during the catalyzed reaction after 2.0 h and dividing by the reaction time and number of acid sites added from either HCl or the carbon catalyst. The calculation is shown in Equation 1:

$$TOF = \frac{Moles\ of\ glucose(sample) - Moles\ of\ glucose\ (blank)}{Added\ Acid\ \times time} \quad (1)$$

Additionally, non-milled microcrystalline cellulose as well as non-milled acidulated cellulose (0h-N-ABMC) and 2h-G-ABMC were reacted for up to 1.0 h at 165 °C over the SO_3H-3DOm carbon catalyst.

The glucose yield is calcuated using Equation 2:

$$Glucose\ Yield = \frac{(Final\ moles\ of\ glucose - moles\ of\ glucose\ added\ by\ coimpregnation)}{Moles\ of\ glucose\ in\ cellulose} \times 100\% \quad (2)$$

The catalyst was recycled and used up to three times to test its resuablity. After each reaction the carbon catalyst was placed in 70 °C water for 1.0 h followed by filtration and washing with 2.0 L of 70°C water. The resulting carbon catalyst was dried overnight at 70 °C and used for the next reaction.

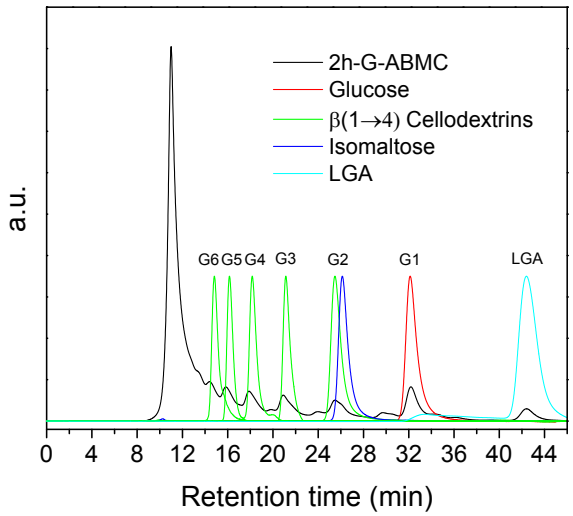

Fig. S1 HPLC Chromatagrams from 2h-G-ABMC, glucose (G1), isomaltose (G2) and the cellodextrins cellobiose (G2), cellotriose (G3), cellotetraose (G4), cellopentaose (G5) and cellohexaose (G6) as well as levoglucosan (LGA) are shown.

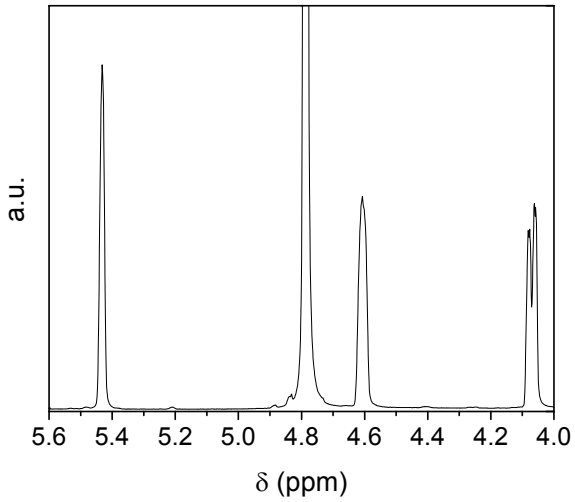

Fig. S2 ^{1}H-NMR spectrum of LGA in D_2O.

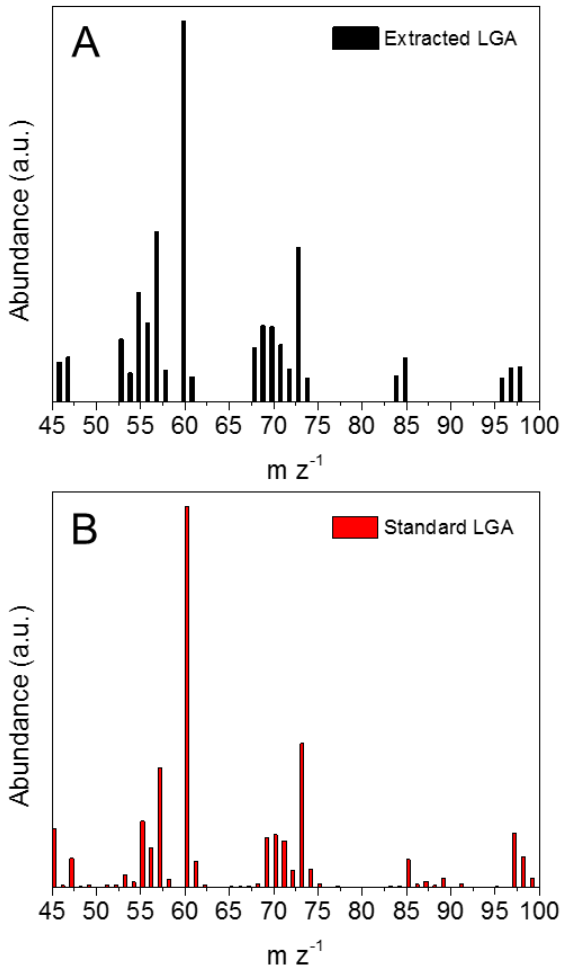

Fig. S3 Mass spectra of A) LGA collected by fractionation of 2h-G-ABMC and B) standard LGA sample.

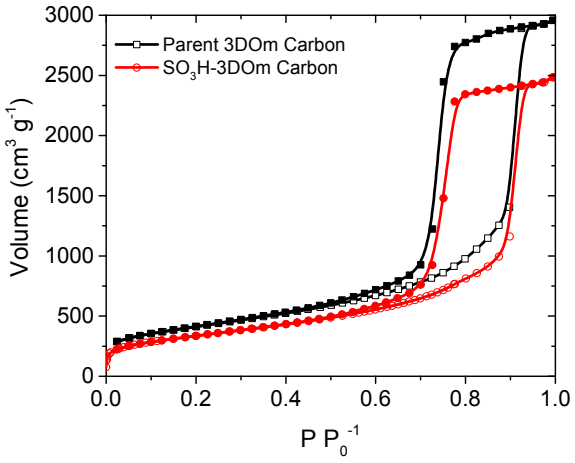

Fig. S4 Nitrogen physisorption isotherms of parent 3DOm carbon and SO_3H 3DOm carbon catalyst at 77 K.

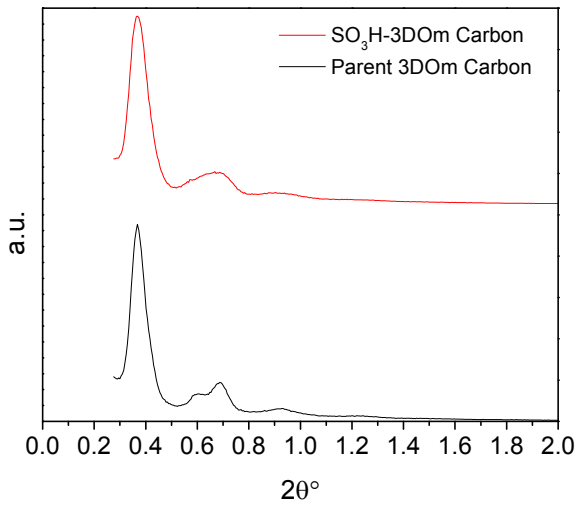

Fig. S5 SAXS of 3DOm carbon and SO_3H 3DOm carbon catalyst.

Table S1 Textural properties of SO_3H-caron

Sample	S_{BET}[1] $m^2\ g^{-1}$	$V_{total}\ p_{ore}$[1] $cm^3\ g^{-1}$	Acid Sites[2] mmol g^{-1}
SO_3H-3DOm Carbon	1191	3.84	0.57
Parent-3DOm Carbon	1445	4.58	N/A

[1]Measured by Nitrogen desorption.

[2]Measured by NaCl ion exchange followed by NaOH titration.

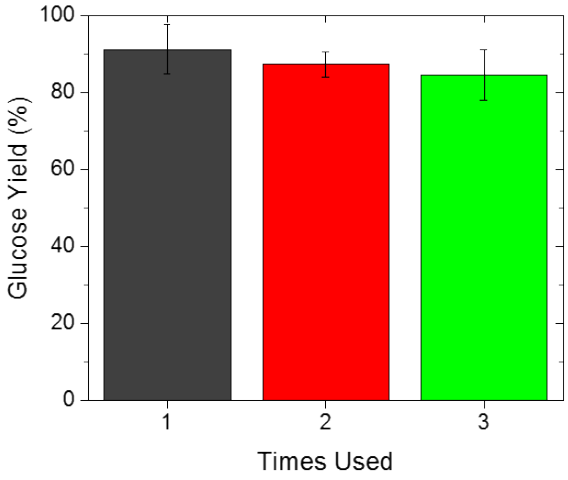

Fig. S6 Repeated reactions using the carbon catalyst at 165 °C using 3.0 mL water, 30 mg 2h-G-ABMC, 20 mg 3DOm-carbon catalyst for 1 h. Error bars present a 95% confidence interval of the average soluble portion.

References

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2. X. Wang, R. Liu, M. M. Waje, Z. Chen, Y. Yan, K. N. Bozhilov and P. Feng, *Chem. Mat.*, 2007, 19, 2395-2397
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