Supporting Information

Adsorption-enhanced Hydrolysis of Glucan Oligomers into Glucose over Sulfonated Three-Dimensionally Ordered Mesoporous Carbon Catalysts

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SAXS:

The d-spacing was calculated using Bragg's law using the first (111) reflection peak of the FCC lattice as shown in Equation S1:

$$n\lambda = 2dsin(\theta) \qquad (S1)$$

Where λ is the wavelength (1.54 Å), n is the whole number of wavelengths (using first reflection $n = 1$), d is the d-spacing and 2θ is the reflection angle. For the (111) plane, the center-to-center distance was calculated from the d-spacing using Equation S2:

$$\text{center to center distance} = \frac{d\sqrt{6}}{2} \qquad (S2)$$

Bayesian inference prior model:

Bayesian inference was performed using the method described in Hummer *et al.*.[1] Each of the five peaks has three parameters which are peak location, peak width and peak intensity. The peak placement variation was pinned to a Gaussian distribution with standard deviation of 5 cm^{-1} with an average value of the initial peak position. The initial guess of peak positions were determined by literature. The parameter of peak width is defined as one quarter of the peak width at one half intensity. The peaks are assumed to be Lorentzian in shape. The initial guesses of parameters used in the prior distribution are shown in Table S1.

Table S1 Prior model parameters for Bayesian inference peak fitting of Raman spectroscopy

Peak	Peak placement (cm^{-1})	¼ peak width at ½ intensity (cm^{-1})	Intensity
G1	1580	1	100% average intensity
D1	1350	1	100% average intensity
D2	1620	1	100% average intensity
D3	1500	1	10% average intensity
D4	1200	1	10% average intensity

Adsorption experiments:

Adsorption isotherms of glucose and cellobiose on the carbon samples were achieved at 0, 20, 50 and 70 °C with concentrations ranging from 1 to 50 mg mL^{-1}. Adsorption of mixed glucan oligomers were measured at room temperature with three different initial concentrations, 1, 10 and 50 mg mL^{-1}. The adsorption was performed in a 2 mL septum-sealed vial. After mixing the carbon and adsorbate, the vials were sealed and placed on a stir-plate at 1000 rpm for 24 h. The solutions were filtered as they were taken out from the vials with syringe filters (220 nm polyethersulfone syringe filters). Tha amount of carbron and adsorbate used in the adsorption is shown in Table S2.

Table S2 Adsorption parameters used in the adsorption measurement.

Cellobiose and mixed oligomer adsorption			Glucose adsorption		
Weight of carbon (g)	Weight of adsorbate (g)	Weight of solution (g)	Weight of carbon (g)	Weight of adsorbate (g)	Weight of solution (g)
0.0041	0.00078	0.7816	0.0034	0.00074	0.7431
0.0057	0.00231	0.7804	0.0044	0.00214	0.7379
0.0064	0.00381	0.7746	0.0046	0.00367	0.739
0.0084	0.00744	0.7742	0.0044	0.00720	0.7343
0.0148	0.01471	0.7734	0.005	0.01408	0.7265
0.0234	0.02611	0.7785	0.0056	0.02474	0.7392
0.0263	0.03490	0.7398	0.0067	0.03494	0.7476

Adsorption isotherm fitting

Langmuir model:

The Langmuir model is shown in Equation S3:

$$Q_e = \frac{Q_{mL} K_L C_{Ae}}{1 + K_L C_{Ae}} \qquad (S3)$$

where Q_e is the equilibrium loading of the adsorbate on the adsorbent, Q_{mL} is the maximum loading, K_L is the Langmuir constant proportional to the ratio of adsorption/desorption rate constants, and C_{Ae} is the equilibrium concentration. As discussed in the manuscript, isotherms used for the calculation were corrected for real adsorption. The parameters were calculated by the least squares method.

Table S3 Langmuir fitting parameters for the adsorption of glucose, cellobiose and mixed glucan oligomers with different chain lengths on the carbon samples at room temperature (20 °C).

	Parent-3DOm Carbon			SO_3H-3DOm Carbon		
Adsorbate	K_L (mL/g)	Q_{mL}(mg/g)	R^2	K_L (mL/g)	Q_{mL}(mg/g)	R^2
Glucose	0.08	285.1	0.997	0.06	120.1	0.994
Cellobiose	1.64	357.2	0.898	0.74	225.3	0.968
Mixed oligomers	4.03	834.2	0.9947	4.73	492.2	0.938

Freundlich model:

The Freundlich model is shown in Equation S4:

$$Q_e = K_{FR} C_{Ae}^{n_{FR}} \qquad (S4)$$

where Q_e is the equilibrium loading of the adsorbate on the adsorbent, C_{Ae} is the equilibrium concentration, K_{FR} and n_{FR} are the adjustable parameters for the Freundlich model. The parameters were calculated by the least squares method.

Table S4 Freundlich fitting parameters for the adsorption of glucose, cellobiose and mixed glucan oligomers with different chain lengths on the carbon samples at room temperature (20 °C).

	Parent-3DOm Carbon			SO_3H-3DOm Carbon		
Adsorbate	K_{FR}	n_{FR}	R^2	K_{FR}	n_{FR}	R^2
Glucose	31.3	0.58	0.993	12.3	0.61	0.993
Cellobiose	226.4	0.18	0.982	117.2	0.23	0.985
Mixed oligomers	574.7	0.16	0.866	352.4	0.13	0.903

The unit of K_{FR} is $mg^{(1-nFR)}mL^{nFR}g^{-1}$

Redlich–Peterson model:

The Redlich–Peterson model is shown in Equation S5:

$$Q_e = \frac{K_{RP} C_{Ae}}{1 + b_{RP} C_{Ae}^{n_{RP}}} \qquad (S5)$$

where Q_e is the equilibrium loading of the adsorbate on the adsorbent, C_{Ae} is the equilibrium concentration, $K_{RP,}$ b_{RP} and n_{RP} are the adjustable parameters for the Redlich–Peterson model. The parameters were calculated by the least squares method.

Table S5 Redlich–Peterson fitting parameters for the adsorption of glucose, cellobiose and mixed glucan oligomers with different chain lengths on the carbon samples at different room temperatures.

	Cellobiose Parent-3DOm				Cellobiose SO_3H-3DOm				Glucose Parent-3DOm				Glucose SO_3H-3DOm			
T(°C)	K_{RP} (L/mol)	b_{RP}	n_{RP}	R^2	K_{RP} (L/mol)	b_{RP}	n_{RP}	R^2	K_{RP} (L/mol)	b_{RP}	n_{RP}	R^2	K_{RP} (L/mol)	b_{RP}	n_{RP}	R^2
0	782.11	5.45	0.918	0.997	575.4	4.88	0.856	0.992	22.95	0.116	0.973	0.997	21.99	0.035	1.181	0.994
20	549.95	6.42	0.886	0.994	395.57	5.35	0.814	0.993	17.91	0.137	0.881	0.996	16.74	0.107	0.912	0.997
50	355.89	2.93	0.888	0.995	250.65	2.3	0.797	0.999	12.35	0.127	0.857	0.992	11.86	0.087	0.902	0.997
70	270.85	2.58	0.884	0.99	193.52	1.39	0.841	0.996	10.06	0.094	0.881	0.994	9.79	0.061	0.921	0.998

Excess adsorption calculations:

Calculations for the excess adsorption were performed using Equation 2 in the manuscript. The specific molar volume of the adsorbent at the experimental temperature, $\bar{V}_A$, were estimated using a combination of Schroeder's and Gain's method for glucose and cellobiose. Schroeder's method is shown in Equation S6.

$$\bar{V}_b = \sum_i n_i \cdot v_{b,i} \qquad (S6)$$

where $\bar{V}_b$= molar volume at normal boiling point in $cm^3\ mol^{-1}$, n_i = the number of features i in the molecule, and $v_{b,i}$ = contribution of feature i molar volume in $cm^3\ mol^{-1}$. In the case of glucose and cellobiose, $v_{b,i}$ of C, H and O = 7 and $v_{b,i}$ of a ring = -7. For example: The molecular formula of cellobiose is $C_{12}H_{22}O_{11}$. The molar volume at normal boiling point of cellobiose is:

$$\bar{V}_b = [(12\ C\ x\ 7) + (22\ H\ x\ 7) + (11\ O\ x\ 7) - (2\ rings\ x\ 7)] = 301\ cm^3\ mol^{-1}$$

The molar volume at normal boiling point is used to calculate the molar volume at a given temperature using Gain's method as shown in Equation S7:

$$\rho_A = \frac{M}{\bar{V}_b}\left[3 - 2\left(\frac{T}{T_b}\right)\right] \qquad (S7)$$

where ρ_A is the density of the adsorbate at temperature T in g cm^{-3}, M is the molecular mass in g mol^{-1}, T_b is the boiling point temperature in K. The molar volume $\bar{V}_A$ in $cm^3\ mol^{-1}$ is calculated by dividing ρ by the molecular mass. T_b for glucose, cellobiose, cellotriose and cellotetraose were estimated by Chemspider to be 527 K, 941 K, 1138 K and 1268 K respectively. The molar volume of cellobiose at 20 °C is calculated as follows:

$$\rho_A = \frac{342\ g\ mol^{-1}}{301\ cm^3 mol^{-1}}\left[3 - 2\left(\frac{298\ K}{941\ K}\right)\right] = 1.485\ g\ cm^{-3}$$

$$\bar{V}_A = \frac{342\ g\ mol^{-1}}{1.485\ g\ cm^{-3}} = 230.5\ cm^3 mol^{-1}$$

Catalyst stability

The stability of the sulfonic acid groups on the carbon was explored by both hydrothermal treatment of sulfonated carbon as well as by repeated testing. Repeated reactions were performed with 3.0 mL of water, 30 mg of mixed glucan oligomers and 20 mg of SO_3H-3DOm carbon catalyst for 2 h at 120 °C. The catalyst was recycled and used up to six times to test its

reusability. 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. The performance of the catalyst after repeated use is shown in Figure S1a. For the hydrothermal treatment, 0.1 g of the SO_3H-3DOm carbon containing 0.89 mmol SO_3H g^{-1} was added to 20 mL of water and treated in an autoclave at 200 °C for up to 5 days. The resulting number of acid sites is shown in Figure S1b.

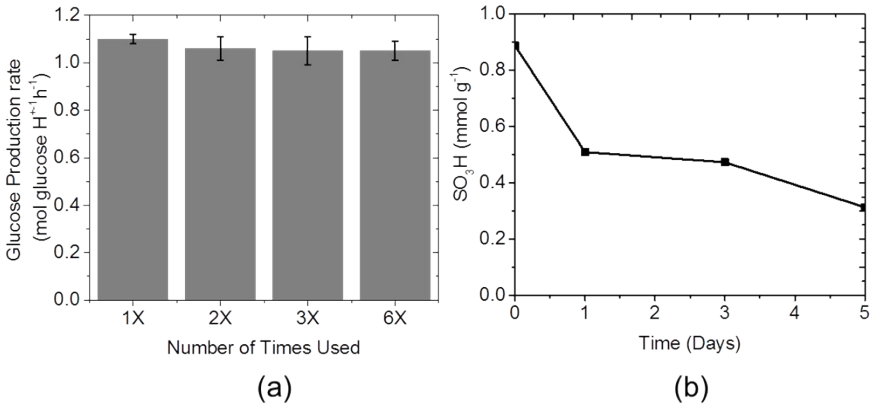

Figure S1 (a) Reusability of SO_3H-3DOm carbon catalyst for hydrolysis of cellobiose (2 h at 120 °C). (b) Hydrothermal stability of SO_3H-3DOm carbon at 200 °C in pure water for up to 5 days.

Elemental analysis:

Elemental analysis including C, S and N for the SO_3H-3DOm carbon catalyst with 0.50 mmol g^{-1} of SO_3H groups (determined by the titration method) was performed at Atlantic Microlabs, Norcross, GA, USA. The weight ratio of S was 1.69 wt.%. The ratio of S to N was 9.2.

Chain-length analysis of large oligomers:

The mixture of soluble oligomers produced from the ball-milling of cellulose co-impregnated with glucose and acid. The Large oligomer portion (chain length > 7 AGUs) was

fraction collected over HPLC. The oligomers were purified by drying on 50 °C hotplate with airflow over the liquid surface over a period of 3 h. ^{1}H-NMR was performed on a Bruker Advance 400 (400 MHz) spectrometer to determine the prevalence of glycosidic linkages and reducing ends. Samples for ^{1}H-NMR were prepared by dispersing 5.0 wt.% dried oligomers 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 resulting ^{1}H-NMR spectrum is shown in Figure S2. The peak of the reducing ends as well as the α(1→6) and β(1→4) glycosidic linkages were integrated. The total chain-length was calculated by determining the relative number of α(1→6) and β(1→4) glycosidic linkages relative to the number of reducing ends. The total chain-length was calculated by first finding the ratio of β(1→4) glycosidic linkages to reducing end by dividing the area of the β(1→4) glycosidic linkage peak ($A_{\beta(1\rightarrow4)}$) by the combined area of the two reducing end peaks (A_{RE}). 1 was added to the β(1→4) glycosidic linkages to reducing end ratio to give the total length of the β(1→4) glycosidic linkage backbone (including the one AGU containing a reducing end). Next, the number of branches per chain was determined by dividing the area of the α(1→6) peak ($A_{\alpha(1\rightarrow6)}$) by the combined area of the two reducing ends. The total calculation is shown in Equation S8:

$$Total\ Chain\ Length = \left(\frac{A_{\beta(1\rightarrow4)}}{A_{RE}} + 1\right) + \frac{A_{\alpha(1\rightarrow6)}}{A_{RE}} \quad (S8)$$

It was found from standards of glucose and cellobiose that the area of peaks in ^{1}H-NMR are proportional to the number of hydrogens present. It was found that the average oligomer contained 14.5 AGUs per chain with an average of 1.65 branches per chain.

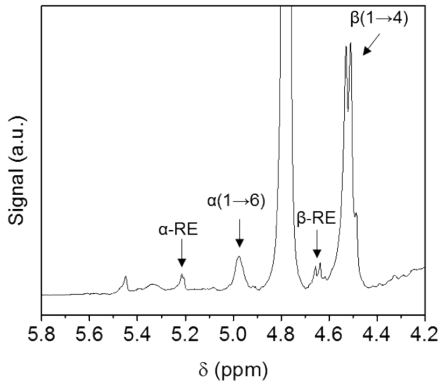

Figure S2 ^{1}H-NMR of fractionated oligomers produced from 1 h milling of cellulose co-impregnated with acid and 12.5% glucose. Reducing end (RE) and linkage peaks are labeled.

References:

1. G. Hummer, New J. Phys., 2005, 7, 34.