Supplementary Information

Production of High-Yield Short-Chain Oligomers from Cellulose via Selective Hydrolysis in Molten Salt Hydrates and Separation

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1. Oligomers molecular weight calculation method

During derivatization, the hydroxy groups of the oligomers were modified with phenyl isocyanate as shown in the Scheme 1. In the scheme, *n* presents the amount of glucose units in oligomers. During the derivation process, phenyl isocyanate reacts with the hydroxy group. The molecular weight of the modified oligomers reflects the original oligomers and the introduced phenyl isocyanate. The former is calculated as (162**n*+18) while the latter is calculated as ((*n*-2)*3*119 + 2*4*119) = (357**n*+238). So the total molecular weight of the products are: 519**n*+256.

Through calculation, the degree of polymerization (DP) was calculated. The molecular weight and DP of oligomers is listed in **Fig. 2.** The figure indicates that most of the hydroxy groups on oligomers were modified and the oligomers with the glucose units ranging from 4-11 present a series of peaks with high intensities. Those small peaks with lower intensities are the oligomers with un-modified hydrogen groups, which means that if the oligomers have α unmodified hydroxy groups, the total molecular weight detected should be 519**n*+256-119**α*.

The relationship between oligomer DP, the theoretical molecular weight of the modified oligomer (M_{wt}) with different glucan units and the detected molecular weight of the oligomer (M_w) by

MALDI are listed in Table S1. It is easy to find that M_w is 23 more than M_{wt} in each line, which is due to the effect of matrix detection method. Sodium has been introduced into the sample during matrix detection process, resulting in an increase of 23 (relative atomic mass of Na) in molecular weight.[1]

2. Adsorption isotherm models

Three different adsorption isotherm models were employed to fit the adsorption data including the Langmuir isotherm model (L), the Redlich-Peterson isotherm model (RP) and the Freundlich isotherm model (FR):

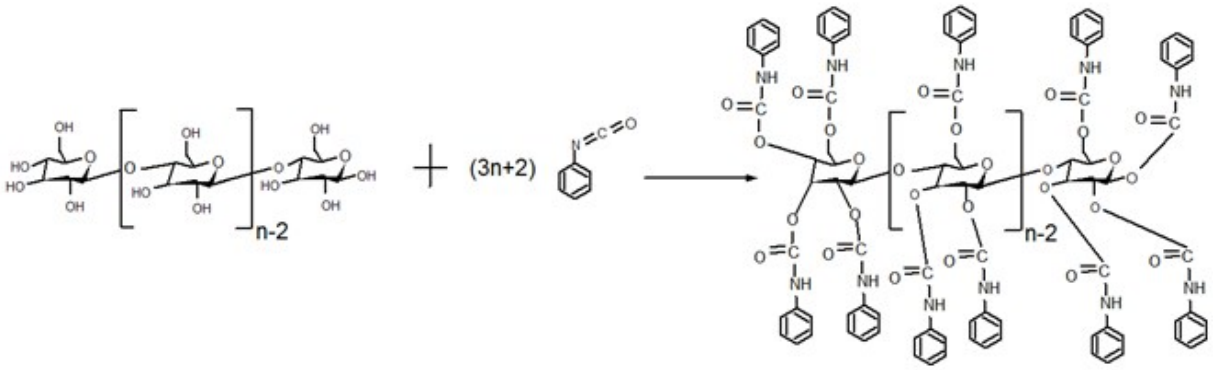
Langmuir: $$Q_e = \frac{Q_{ml}K_L C_{Ae}}{1+KLCAe}$$

Redlich-Peterson: $$Q_e = \frac{K_{RP}C_{Ae}}{1+b_{RP}C_{Ae}^{n_{RP}}}$$

Freundlich: $$Q_e = K_{FR}C_{Ae}^{n_{FR}}$$

Here Q_e is the equilibrium adsorbate loading and C_{Ae} is the equilibrium concentration. Q_{ml} is the maximum loading and K_L is the Langmuir constant proportional to the ratio of adsorption/desorption rate constants for the Langmuir model; K_{RP}, b_{RP} and n_{RP} are the adjustable parameters for the Redlich-Peterson model; K_{FR} and n_{FR} are the adjustable parameters for the Freundlich model. All constant parameters were calculated using the least squares method.

3. Figures



Scheme 1. Derivatization process

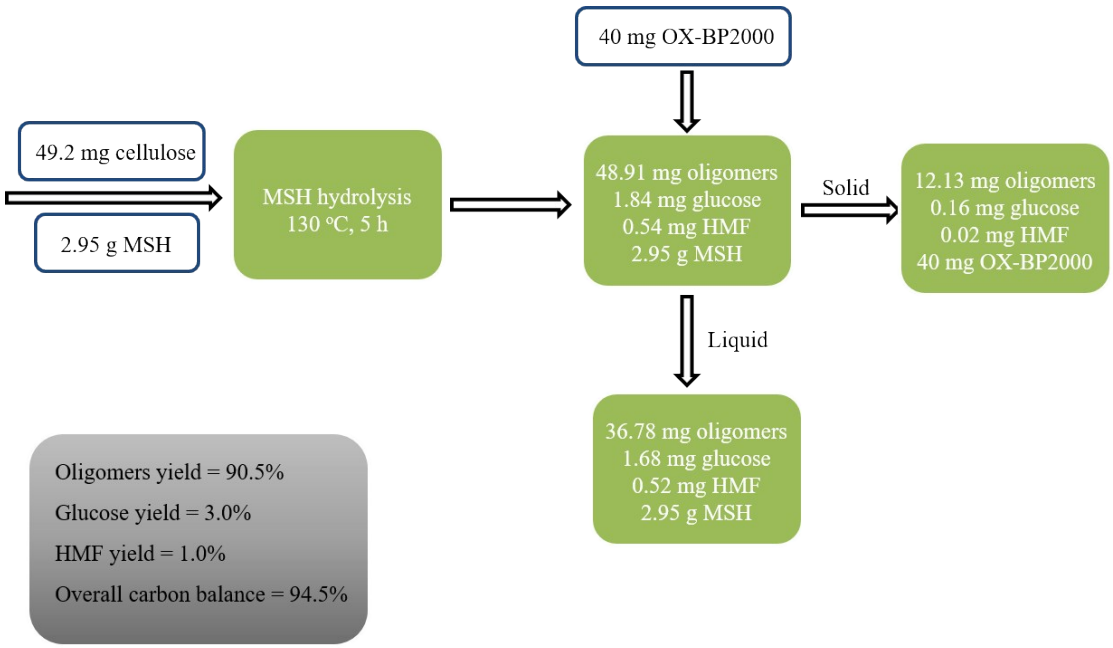


Fig. S1 Flow sheet of cellulose hydrolysis followed by separation.

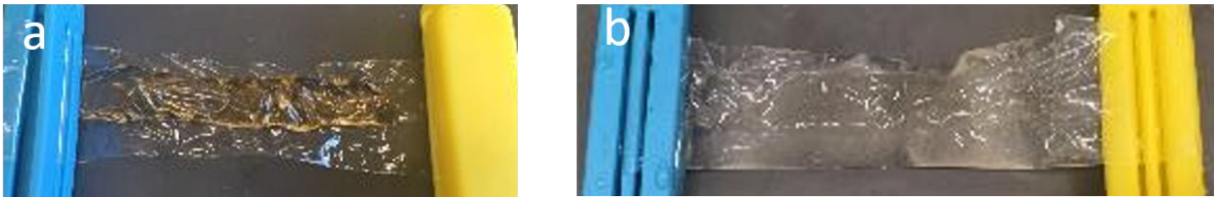


Fig. S2. Pictures of the hydrolysate (a) before and (b) after dialysis.

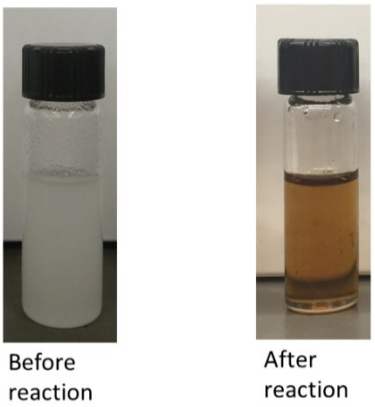


Fig. S3. Photographs of the hydrolysates before and after hydrolysis. Reaction conditions: 500 mg cellulose, 30 g molten salt, 130 °C, 5 h.

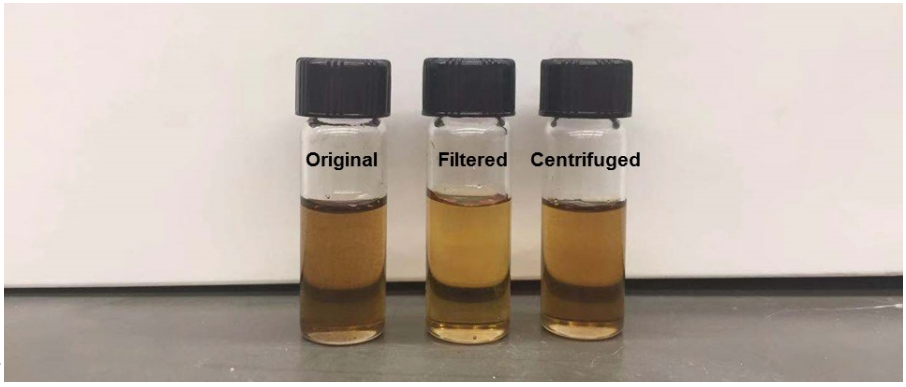


Fig. S4. Photographs of the hydrolysates. Original solution obtained from hydrolysis at reaction conditions: 500 mg cellulose, 30 g molten salt, 130 °C, 5 h; Filtered solution: Original solution filtered with 0.22 μm filter paper; Centrifuged solution: Supernatant liquor obtained from centrifuged original solution at 6,000 rpm for 10 min.

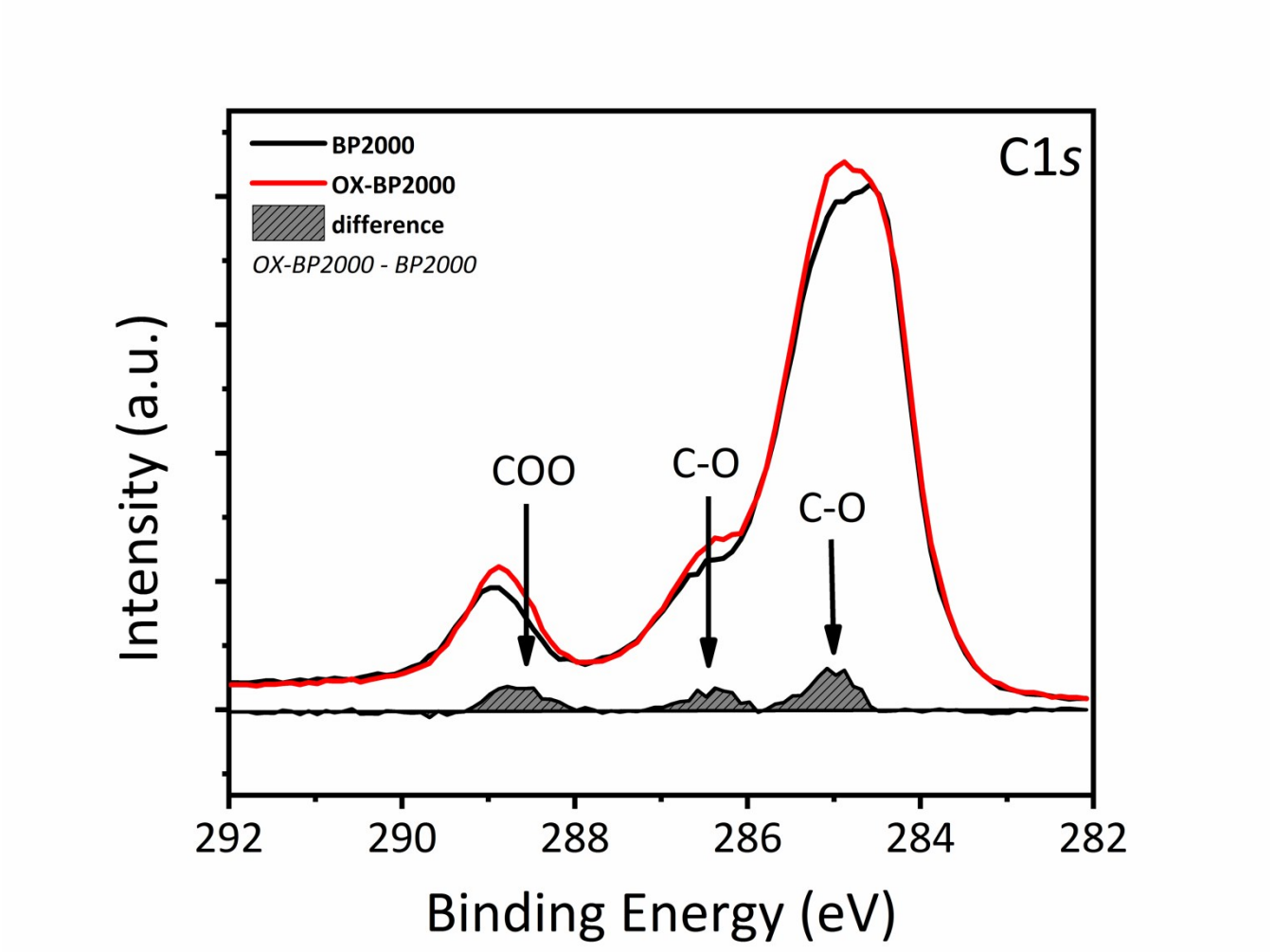


Fig. S5. Normalized C1s XPS spectra of BP2000 and BP2000 (OX-BP2000) after oxidation by H_2O_2. The difference in the two spectra is calculated from subtracting the BP2000 one from the OX-BP2000 one.

Adsorption on activated carbon with Redlich-Peterson equation fitting:

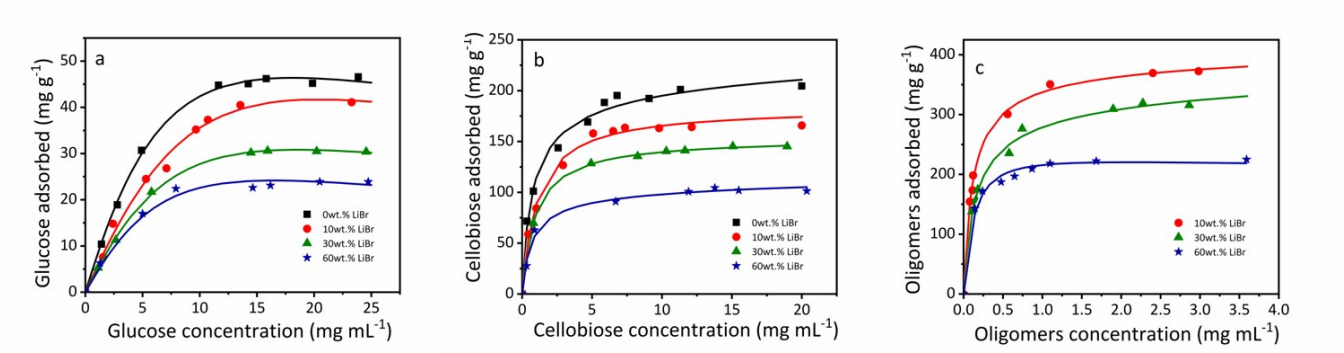


Fig. S6. Adsorption isotherms of (a) glucose, (b) cellobiose and (c) oligomers on activated carbon in the solution with LiBr concentration of 0, 10, 30 and 60 wt.% at room temperature (about 20°C). G_c: glucose concentration; C_c: cellobiose concentration; O_c: oligomers concentration; Y_{carbon}: amount of products adsorbed on carbon. Oligomers preparation: 500 mg cellulose, 30 g molten salt, 130 °C, 5 h. The points are from experimental measurements. The lines are from the Redlich-Peterson equation fitting.

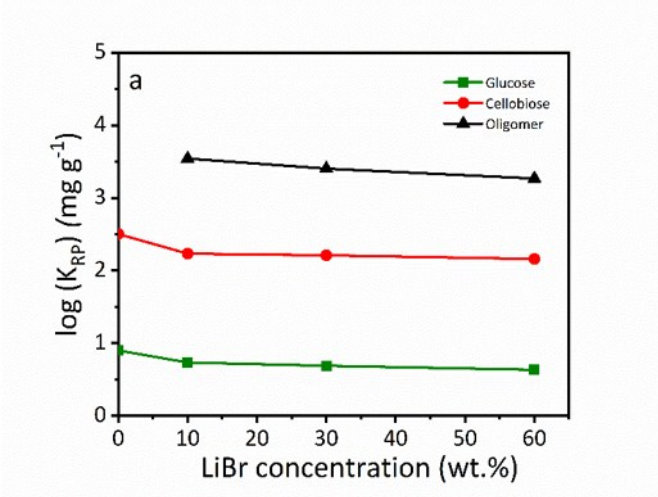
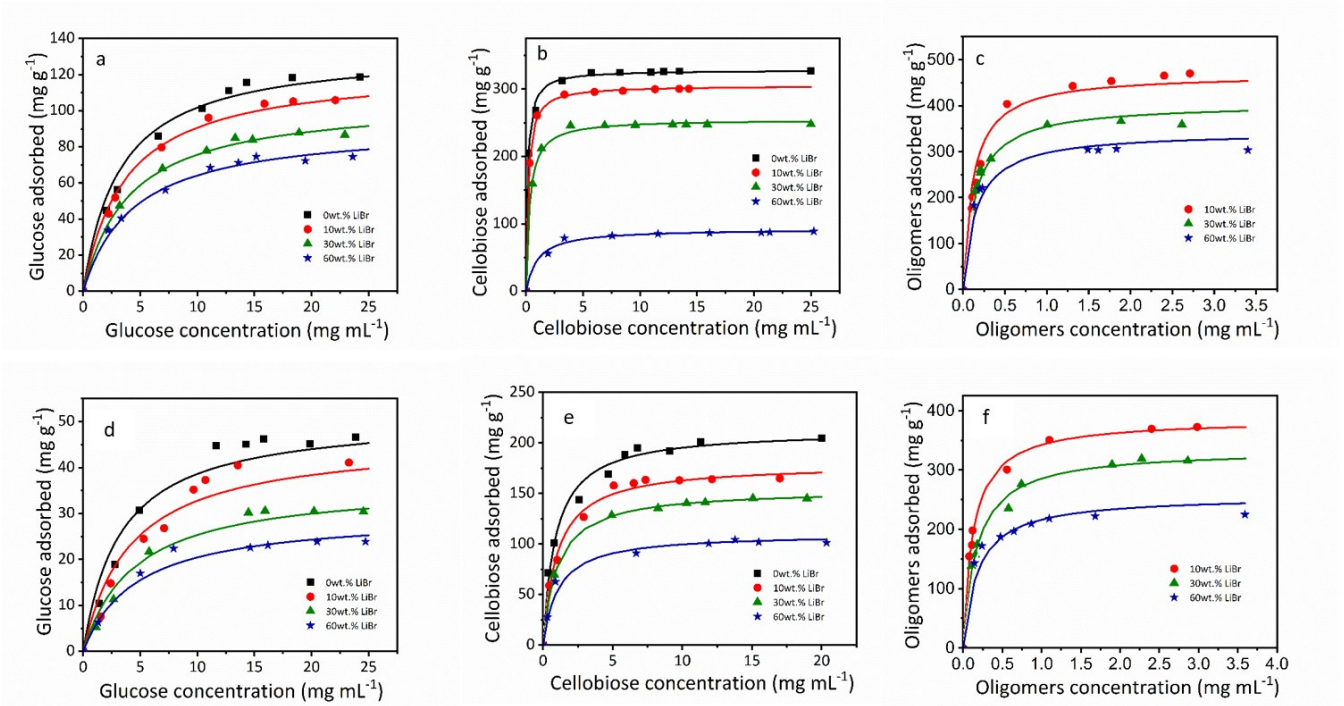


Fig. S7. The effect of LiBr concentration on K_{RP} of activated carbon. Three different adsorbates including glucose, cellobiose and oligomers were investigated. The parameters are from the Redlich-Peterson equation fitting.



Adsorption on OX-BP2000 and activated carbon with Langmuir equation fitting:

Fig. S8. Adsorption isotherms of (a,d) glucose, (b,e) cellobiose and (c,f) oligomers on (a,b,c) OX-BP2000 and (d,e,f) activated carbon in the solution with LiBr concentration of 0, 10, 30 and 60 wt.% at room temperature (about 20°C). G_c: glucose concentration; C_c: cellobiose concentration; O_c: oligomers concentration; Y_{carbon}: amount of products adsorbed on carbon. Oligomers preparation: 500 mg cellulose, 30 g molten salt, 130 °C, 5 h. The points are from experimental measurements. The lines are from the Langmuir equation fitting.

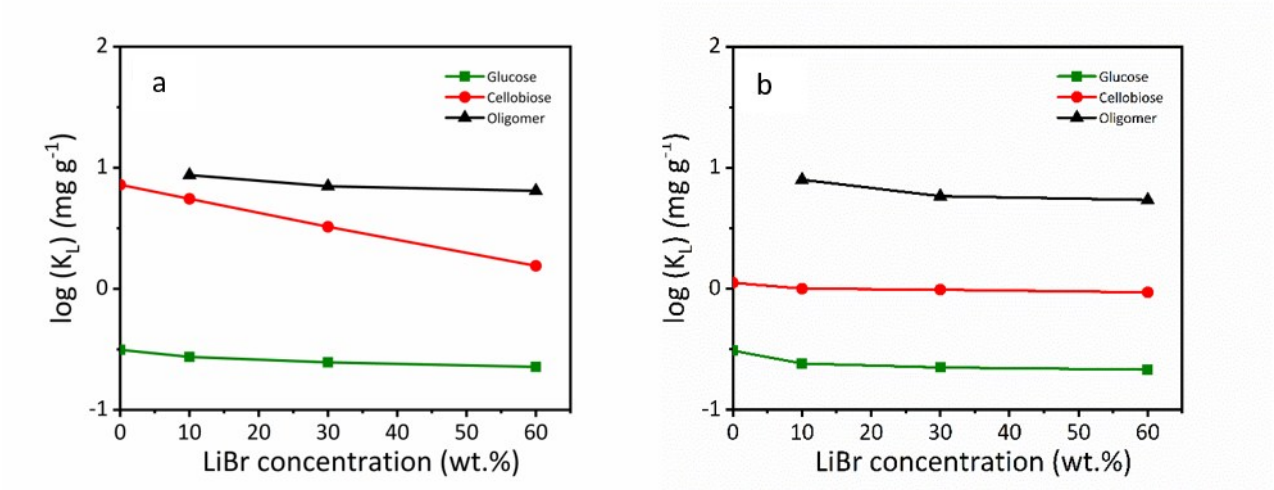


Fig. S9. Effect of LiBr concentration on K_L of (a) OX-BP2000 and (b) activated carbon. Three different adsorbates including glucose, cellobiose and oligomers were investigated. The parameters are from the Langmuir equation fitting.

Adsorption on OX-BP2000 and activated carbon with Freundlich equation fitting:

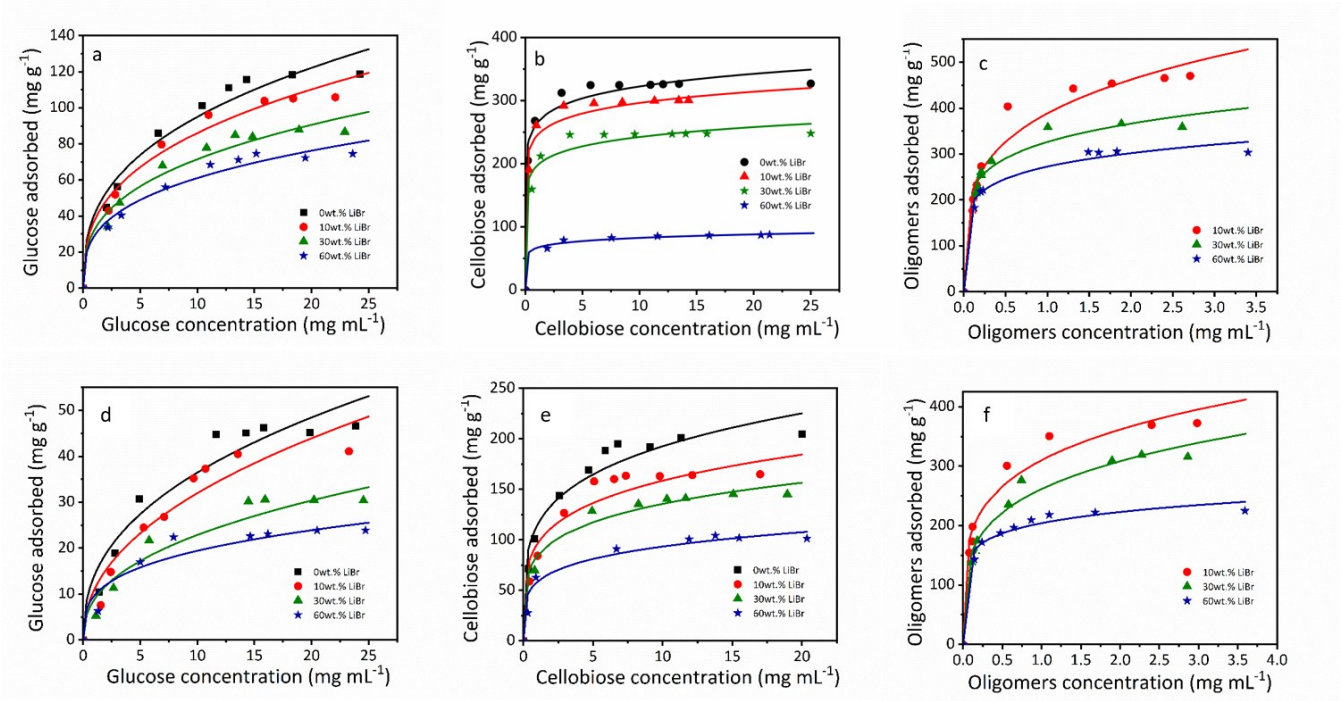


Fig. S10. Adsorption isotherms of (a,d) glucose, (b,e) cellobiose and (c,f) oligomers on (a,b,c) OX-BP2000 and (d,e,f) activated carbon in the solution with LiBr concentration of 0, 10, 30 and 60 wt.% at room temperature (about 20°C). G_c: glucose concentration; C_c: cellobiose concentration; O_c: oligomers concentration; Y_{carbon}: amount of products adsorbed on carbon. Oligomers preparation: 500 mg cellulose, 30 g molten salt, 130 °C, 5 h. The points are from experimental measurements. The lines are from the Freundlich equation fitting.

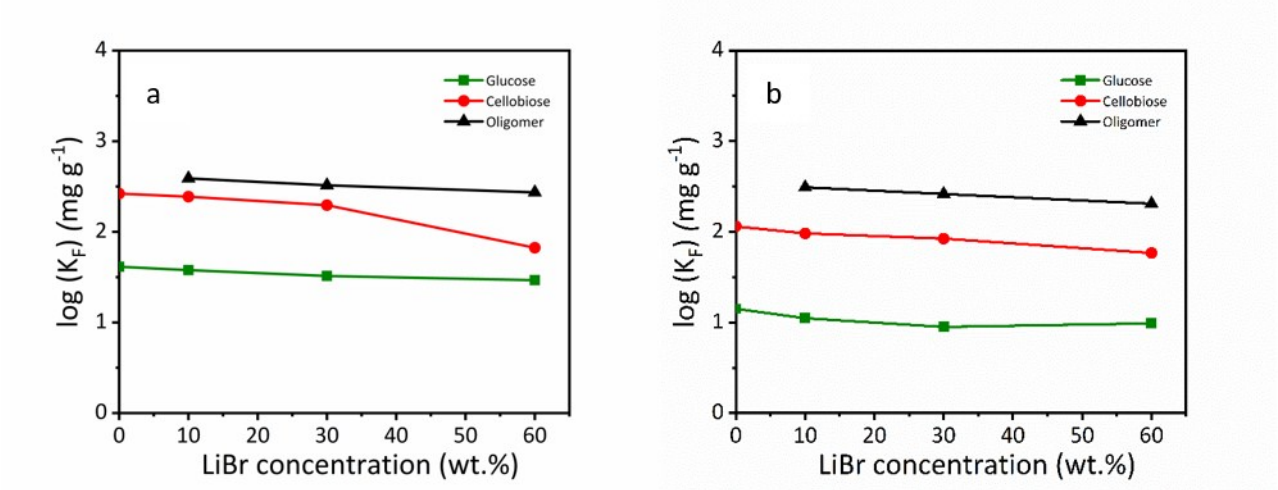


Fig. S11. Effect of LiBr concentration on K_F of (a) OX-BP2000 and (b) activated carbon. Three different adsorbates including glucose, cellobiose and oligomers were investigated. The parameters are from the Freundlich equation fitting.

4. Tables

Table S1. Relationship between oligomer DP, theoretical molecular weight of the modified oligomer (M_{wt}) and detected molecular weight of the oligomer (M_w)

DP	M_{wt}	M_w
4	2332	2355
5	2851	2874
6	3370	3393
7	3889	3912
8	4408	4431
9	4927	4950
10	5446	5469
11	5965	5988

Table S2. Elemental composition in adsorbents.

Materials	C%	O%
BP2000	86.42	13.58
OX-BP2000	85.05	14.95

Table S3. Langmuir fitting parameters for the adsorption of glucose, cellobiose and oligomers on activated carbon at room temperature (20 ^oC).

Adsorbent	Adsorbate	LiBr solution	K_L (mL/g^2)	Q_{ml}	R^2
OX-BP2000	Glucose	0 wt.%	314	134.267	0.963
OX-BP2000	Glucose	10 wt.%	274	123.863	0.989
OX-BP2000	Glucose	30 wt.%	247	106.373	0.988
OX-BP2000	Glucose	60 wt.%	227	92.461	0.973
OX-BP2000	Cellobiose	0 wt.%	7248	328.273	0.980
OX-BP2000	Cellobiose	10 wt.%	5540	305.176	0.997

OX-BP2000	Cellobiose	30 wt.%	3255	255.077	0.976
OX-BP2000	Cellobiose	60 wt.%	1548	90.401	0.964
OX-BP2000	Oligomers	10 wt.%	8711	468.954	0.947
OX-BP2000	Oligomers	30 wt.%	7033	404.919	0.945
OX-BP2000	Oligomers	60 wt.%	6452	343.339	0.963
Activated carbon	Glucose	0 wt.%	309	51.147	0.923
Activated carbon	Glucose	10 wt.%	242	46.324	0.917
Activated carbon	Glucose	30 wt.%	224	36.670	0.972
Activated carbon	Glucose	60 wt.%	215	29.989	0.930
Activated carbon	Cellobiose	0 wt.%	1125	212.697	0.972
Activated carbon	Cellobiose	10 wt.%	1004	179.126	0.979
Activated carbon	Cellobiose	30 wt.%	985	153.990	0.998
Activated carbon	Cellobiose	60 wt.%	936	110.242	0.960
Activated carbon	Oligomers	10 wt.%	7970	385.669	0.992
Activated carbon	Oligomers	30 wt.%	5833	334.732	0.982
Activated carbon	Oligomers	60 wt.%	5425	256.332	0.939

Table S4. Redlich-Peterson fitting parameters for the adsorption of glucose, cellobiose and oligomers on OX-BP2000 and activated carbon at room temperature (20 ^{o}C)

Adsorbent	Adsorbate	LiBr solution	K_{RP} (mL/g)	b_{RP}	n_{RP}	R^2
Activated carbon	Glucose	0 wt.%	7.972	0.030	1.473	0.997
Activated carbon	Glucose	10 wt.%	5.442	0.013	1.602	0.986
Activated carbon	Glucose	30 wt.%	4.895	0.023	1.512	0.999
Activated carbon	Glucose	60 wt.%	4.321	0.028	1.515	0.970
Activated carbon	Cellobiose	0 wt.%	319.703	1.806	0.931	0.981
Activated carbon	Cellobiose	10 wt.%	171.305	0.940	0.998	0.975
Activated carbon	Cellobiose	30 wt.%	162.493	1.075	0.996	0.999
Activated carbon	Cellobiose	60 wt.%	144.766	1.363	1.000	0.983

Activated carbon	Oligomers	10 wt.%	3487.743	9.330	0.962	0.992
Activated carbon	Oligomers	30 wt.%	2534.294	8.090	0.929	0.987
Activated carbon	Oligomers	60 wt.%	1856.314	7.605	1.060	0.989

Table S5. Freundlich fitting parameters for the adsorption of glucose, cellobiose and oligomers on OX-BP2000 and activated carbon at room temperature (20 ^{o}C)

Adsorbent	Adsorbate	LiBr solution	K_F	n_{FR}	R^2
OX-BP2000	Glucose	0 wt.%	41.203	0.363	0.932
OX-BP2000	Glucose	10 wt.%	37.796	0.357	0.946
OX-BP2000	Glucose	30 wt.%	32.631	0.341	0.923
OX-BP2000	Glucose	60 wt.%	29.286	0.319	0.928
OX-BP2000	Cellobiose	0 wt.%	264.117	0.087	0.856
OX-BP2000	Cellobiose	10 wt.%	244.416	0.084	0.794
OX-BP2000	Cellobiose	30 wt.%	196.698	0.091	0.748
OX-BP2000	Cellobiose	60 wt.%	66.752	0.092	0.868
OX-BP2000	Oligomers	10 wt.%	388.662	0.251	0.919
OX-BP2000	Oligomers	30 wt.%	326.411	0.167	0.902
OX-BP2000	Oligomers	60 wt.%	272.702	0.147	0.985
Activated carbon	Glucose	0 wt.%	14.179	0.410	0.905
Activated carbon	Glucose	10 wt.%	11.133	0.458	0.886
Activated carbon	Glucose	30 wt.%	8.922	0.409	0.907
Activated carbon	Glucose	60 wt.%	9.774	0.298	0.833
Activated carbon	Cellobiose	0 wt.%	114.769	0.225	0.919
Activated carbon	Cellobiose	10 wt.%	96.206	0.217	0.846
Activated carbon	Cellobiose	30 wt.%	84.161	0.207	0.912
Activated carbon	Cellobiose	60 wt.%	58.476	0.203	0.904
Activated carbon	Oligomers	10 wt.%	310.305	0.222	0.940
Activated carbon	Oligomers	30 wt.%	261.74	0.237	0.952

Activated carbon	Oligomers	60 wt.%	204.208	0.127	0.978

1. P. Chen, A. Shrotri and A. Fukuoka, ChemSusChem, 2019,12, 1–6