Supporting information for

Glucan Adsorption on Mesoporous Carbon Nanoparticles: Effect of Chain Length and Mesoporosity

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(1) The quantity adsorbed on MCN after adsorption

In the liquid phase as the following equation:

$$q = \frac{(C_0 - C_E)V}{m}$$

,where q is the concentration of sugar on the adsorbed phase, indicated as the quantity of sugar per unit amount of MCN. In addition, C_0 and C_E present the initial and the equilibrium concentration of solute in the liquid phase, and V is the volume of the liquid phase and m is the mass of dry adsorbent.

(2) Langmuir adsorption calculation

Langmuir theory is based on the assumption that the surface of adsorbent is energetically homogenous, and that a monolayer surface coverage is formed with no interactions between the molecules adsorbed. The Langmuir equation:

$$q_e = \frac{q_m b C_e}{(1 + bC_e)}$$

or can be also written in

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e$$

,where q_m (mg.g^{-1}) and b (L.g^{-1}) are the Langmuir constants, representing the maximum adsorption capacity for the solid-phase loading and the energy constant related to the heat

of adsorption, respectively. q_e is the uptake capacity and C_e is the equilibrium concentration.

(3) Calculation of cellobiose footprint from single-crystal X-ray diffraction data

The crystal structure of cellobiose has a reduced unit cell volume of 729.54 $Å^3$ and consists of two cellobiose molecules per unit cell (*Acta Crystallogr*. **1961**, 14, (6), 598-607). This means that each cellobiose molecule occupies a volume of ~365 $Å^3$, which is equivalent to a characteristic footprint of $(365\ Å^3)^{2/3} = 0.51\ nm^2$/cellobiose.

(4) Theoretical cellobiose occupied on MCN per gram

$$\#\ of\ cellobiose\ per\ unit\ area = \frac{1}{0.51} = 1.96\ \frac{cellobiose}{nm^2}$$

$$Total\ mass\ adsorbed\ on\ the\ surface\ of\ MCN$$
$$= \frac{1.96\ \cancel{cellobiose}}{\cancel{nm^2}} * \frac{5.686 * 10^{-22} g}{\cancel{cellobiose}} * 1984\cancel{m^2} * \frac{10^{18}\cancel{nm^2}}{\cancel{m^2}}$$
$$= 2211\ mg$$

(5) The mass occupied into external surface:

Density of MCN $\delta = 0.54\ {}^{g}/_{cm^3}$

Volume of MCN $Vp = \frac{4}{3}\pi R^3 = \frac{4}{3}\pi(10^{-7}m)^3 = 4.189 * 10^{-21} m^3$

Mass of MCN

$$Mp = Vp * \delta = 4.189 * 10^{-21}\cancel{m^3} * 0.54\ \frac{g}{\cancel{cm^3}} * \frac{10^6\cancel{cm^3}}{\cancel{m^3}} = 2.26 * 10^{-15} g$$

Total # of particles (20 mg of MCN)

$$\#p = \frac{Mass\ of\ MCN}{Mp} = \frac{2 * 10^{-2} g}{2.26 * 10^{-15} g} = 8.85 * 10^{12}$$

Total external surface

$$Total\ external\ surface\ area = 4\pi R^2 * \#p$$
$$= 4\pi(10^{-7}m)^2 * 8.85 * 10^{12} = 1.11m^2$$

Theoretical mass adsorbed by external surface

$$Total\ mass\ adsorbed\ by\ external\ surface$$
$$= \frac{1.96\ \cancel{cellobiose}}{\cancel{nm^2}} * \frac{5.686 * 10^{-22}g}{\cancel{cellobiose}} * 1.11\cancel{m^2} * \frac{10^{18}\cancel{nm^2}}{\cancel{m^2}}$$
$$= 1.2mg$$

Experimental mass adsorbed on MCN

$$Total\ adsorbed\ mass = \frac{303mg}{g\ of\ MCN} * 20mg\ of\ MCN * \frac{10^{-3}g}{mg} = 6.06mg$$

$$6.06mg > 1.2mg$$

(6)The change of ΔG

$$\Delta\Delta G = -R.T.\ln\left(\frac{K_{Cb}}{K_{Glu}}\right) = -8.314\times298\times2.4159 = -5986\,{}^{J}/_{Mol}$$
$$= -5.986\,{}^{KJ}/_{Mol} = -1.43\,{}^{Kcal}/_{Mol}$$

$$\Delta\Delta G = -R.T.\ln\left(\frac{K_{Ct}}{K_{Cb}}\right) = -8.314\times298\times2.12 = -5239\,{}^{J}/_{Mol}$$
$$= -5.239\,{}^{KJ}/_{Mol} = -1.58\,{}^{Kcal}/_{Mol}$$

$$\Delta\Delta G = -R.T.\ln\left(\frac{K_{Ct}}{K_{Cb}}\right) = -8.314\times298\times0.34 = -842\,{}^{J}/_{Mol}$$
$$= -0.842\,{}^{KJ}/_{Mol} = -0.41\,{}^{Kcal}/_{Mol}$$

(7) Calibration of the mass of ^{13}C-labeled glucose versus ^{13}C DP-MAS NMR Sigal Intensity

Solid-state ^{13}C DP-MAS NMR spectroscopy is used to close material balances of adsorbed glucan amounts (on a mass of glucan equivalents basis). A calibration is first made by using standard materials consisting of known ^{13}C-labeled glucose concentrations on MCN materials. The ratio of area of glucose (40-110 ppm)/area of TKTMS (Tetrakis(trimethylsilyl)silane) (-4-+4 ppm) as a function of the ratio of the mass of ^{13}C glucose/mass of TKTMS (^{13}C nature abundance 1.1%) is shown in Figure S1, and is linear. The calibration line in Figure S1 allows the mass of ^{13}C-labeled glucan adsorbed on a MCN material to be calculated, based on the measured solid-state ^{13}C DP-MAS NMR signal intensity.

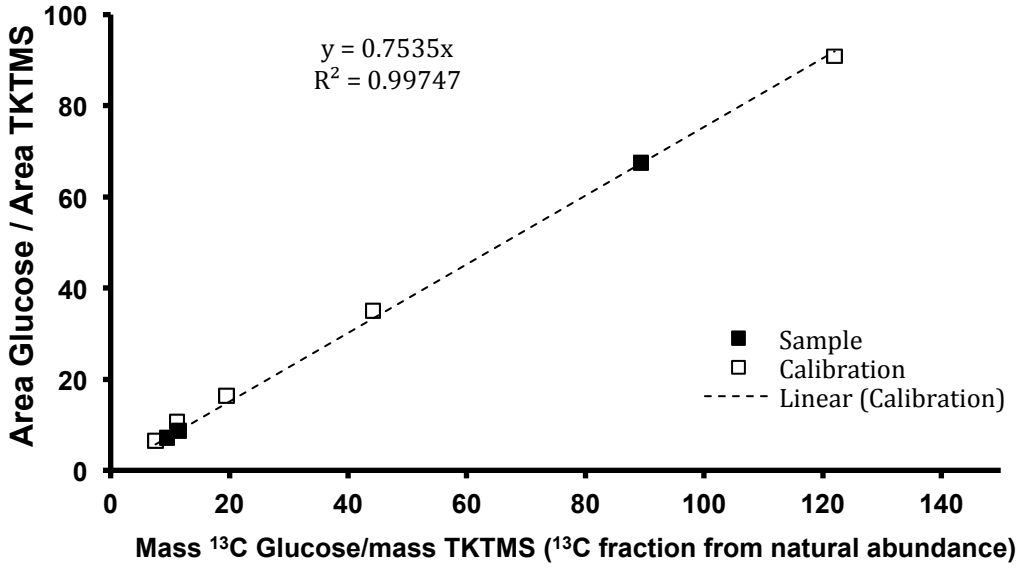

Figure S1. Calibration of the mass of ^{13}C glucose for ^{13}C DP/NMR

(8) The external surface of carbon nanopowder (CNP)

The mass occupied into external surface (CNP):

$$\frac{1}{\delta} = \frac{Volume}{g\ C} = \frac{pore\ Volume}{g\ C} + \frac{C\ Volume(non-pore)}{g\ C} = 0.22 + \frac{1}{2.267}$$
$$= 0.66$$

Density of MCN $\delta = 1.52\ {}^{g}/_{cm^3}$

Volume of CNP $Vp = \frac{4}{3}\pi R^3 = \frac{4}{3}\pi(2.5 * 10^{-8}m)^3 = 6.545 * 10^{-23}m^3$

Mass of CNP

$$Mp = Vp * \delta = 4.189 * 10^{-21}\cancel{m^3} * 1.52\ \frac{g}{\cancel{cm^3}} * \frac{10^6\cancel{cm^3}}{\cancel{m^3}} = 9.95 * 10^{-17}g$$

Total # of particles (1g of MCN)

$$\#p = \frac{Mass\ of\ MCN}{Mp} = \frac{1g}{9.95 * 10^{-17}g} = 1 * 10^{16}$$

Total external surface

$$Total\ external\ surface\ area = 4\pi R^2 * \#p$$
$$= 4\pi(2.5 * 10^{-8}m)^2 * 1 * 10^{16} = 78.5m^2$$

(9) X-ray Photoelectron Spectroscopy (XPS) analysis of MCN

The goal of XPS analysis of MCN materials is to characterize the chemical state of carbon comprising the MCN both before and after the treatment with concentrated HCl (37 wt%, aqueous) for 10 min at room temperature .The C1s signal is broad and can be deconvoluted into hydrocarbon and oxidized carbon species, which include alcohol/ether, carbonyl and carboxyl contributors as listed in Table S1. The concentrations of oxidized carbon in MCN and MCN after concentrated HCl treatment are 17.9 atom % and 16.9 atom %, respectively, and the dominant functional groups on MCN are hydrocarbons for both cases (~77 atom %). Data in Table S1 show little to no change in the proportion of carbon present including hydrocarbon, alcohol/ether, carbonyl, and carboxyl as a result of concentrated HCl treatment. A very slight increase in chloride concentration (less than 0.1%) is observed after concentrated HCl treatment.

Binding Energy (eV)	Atom Concentration (%)	
	MCN	MCN treated after HCl (10 min)
Hydrocarbon* (284.6±0)	77.59±0.67	77.36±0.40
Alcohol/Ether (285.7±0)	11.53±0.14	10.63±0.23
Carbonyl (286.8±0)	4.12±0.12	4.12±0.11
Carboxyl (288.0±0.1)	2.25±0.31	2.16±0.09
Chloride (200.5±0.9)	0.00±0.01	0.09±0.02

* The shake-up satellite peak (289.8 eV) due to carbon π-π* transition was observed but ignored in this analysis.

Table S1. Atom concentration of binding energy of C1s and Cl 2p3/2 by X-ray Photoelectron Spectroscopy

(10) Adsorption isotherm of cellotriose and cellotetraose on MCN

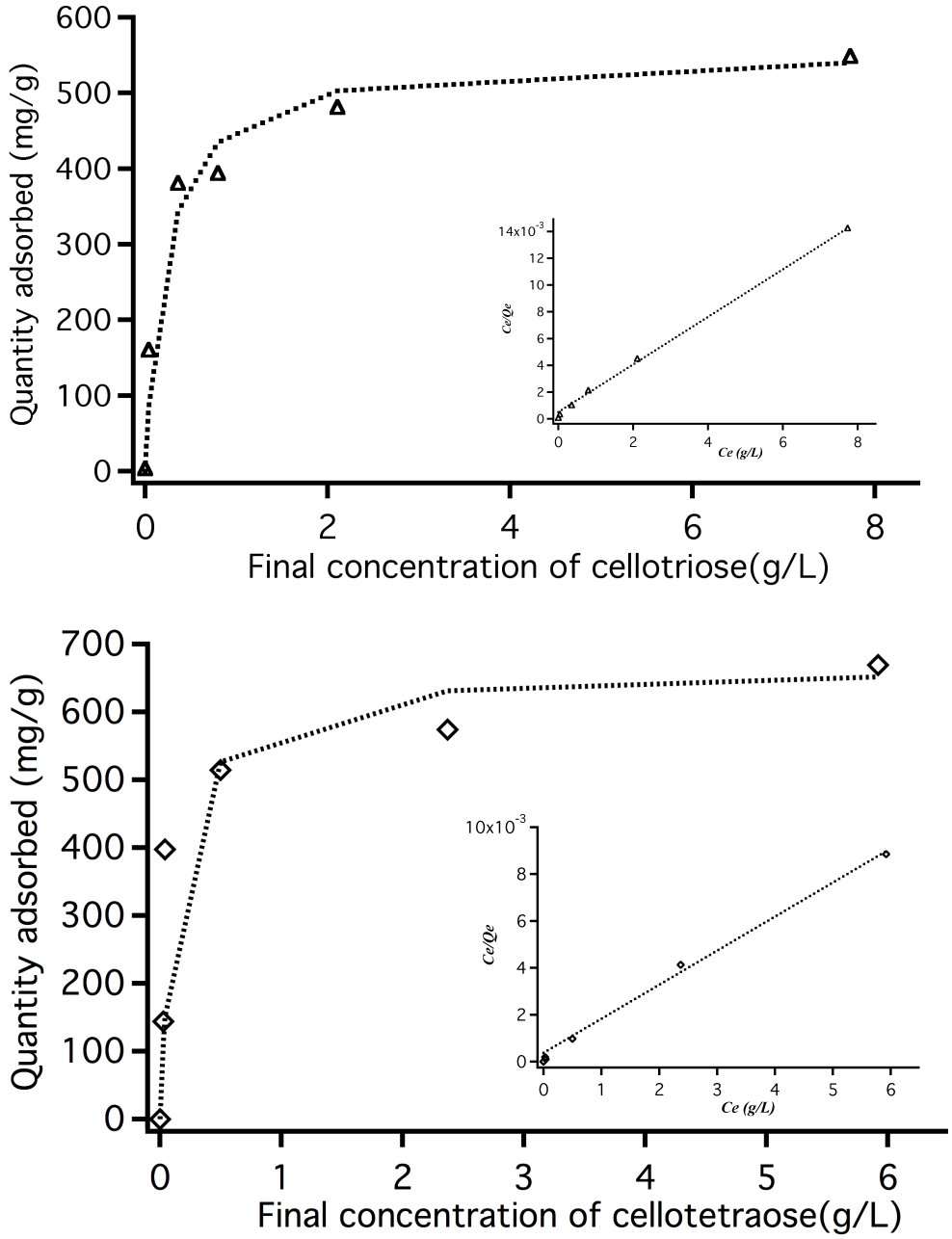

Figure S2. Adsorption isotherms of cellotriose (top) and cellotetraose (bottom) on MCN. The dotted line is a nonlinear fit based on the Langmuir isotherm equation. Inset: Isotherm data represented using transformed coordinates, which are used for obtaining best-fit Langmuir isotherm parameters via linear regression.