Supporting Information

Adsorption of Xyloglucan onto Thin Films of Cellulose Nanocrystals and Amorphous Cellulose: Film Thickness Effects

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Provided Supporting Information

I. Representative Data for Xyloglucan (XG) Adsorption onto Cellulose Surfaces

Figure S1. Representative data for the adsorption of xyloglucan solutions of varied concentration onto (A, B) 30 nm d-CNC, (C, D) 13 nm s-CNC, and (E, F) 15 nm RC films by QCM-D (n = 5; A, C, E) and SPR (B, D, E). Symbols correspond to XG concentrations of (●) 1 mg·L^{-1}, (■) 5 mg·L^{-1}, (▲) 10 mg·L^{-1}, (▼) 25 mg·L^{-1}, (◀) 50 mg·L^{-1}, (▶) 75 mg·L^{-1}, (◆) 100 mg·L^{-1}, (✦) 250 mg·L^{-1}, and (◆) 500 mg·L^{-1}.

II. Determination of Surface Concentration (Γ) by QCM-D and SPR Data

Table S1. Values used in the de Feijter equation to convert measured SPR data into surface excesses.

III. Adsorption Isotherm Fitting Parameters

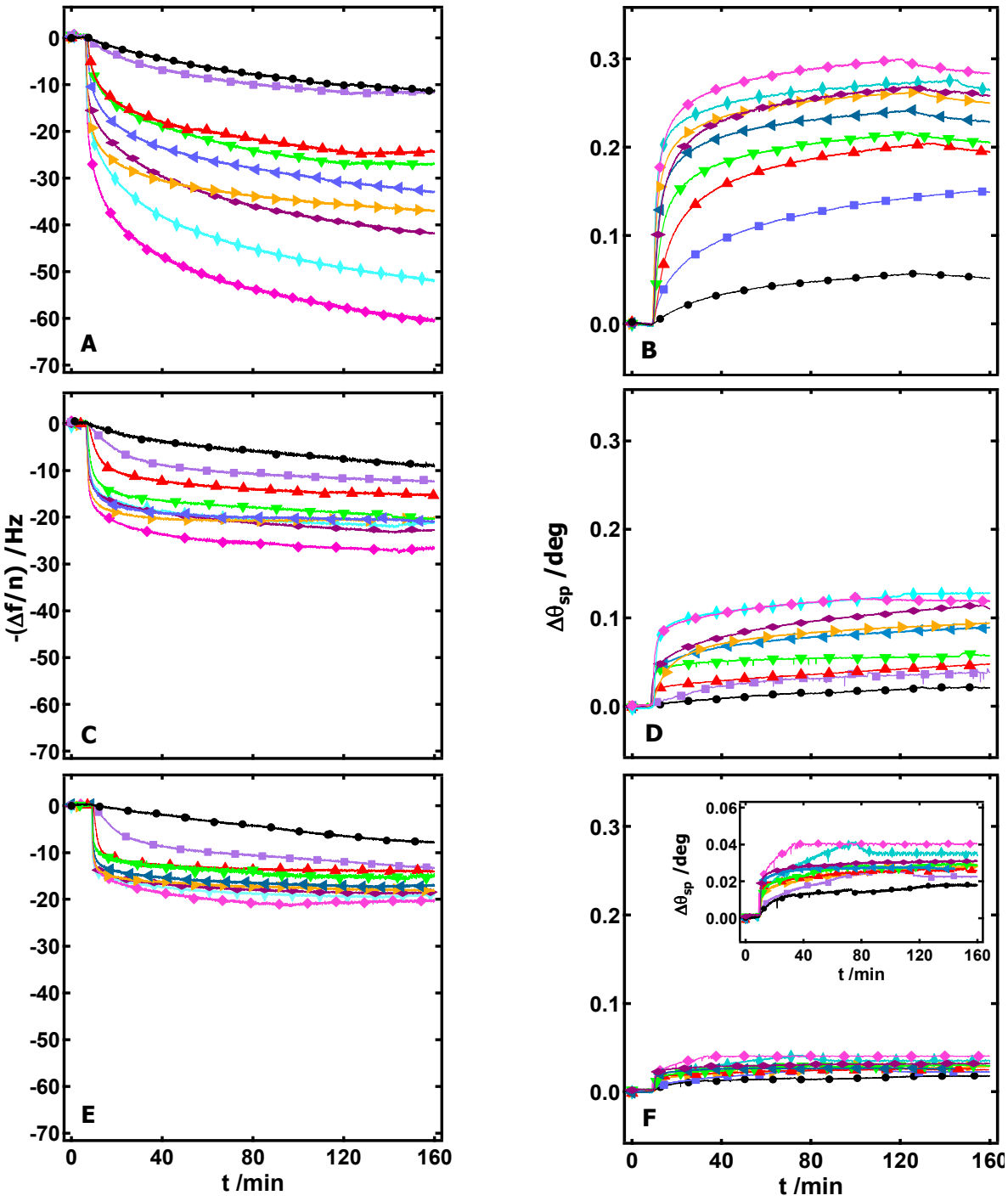
Table S2. Freundlich and Langmuir isotherm fitting parameters for XG adsorbed on RC, s-CNC, and d-CNC films as determined from QCM and SPR data.

IV. Roughness and Aggregate Heights of Model Surfaces

Figure S2 Representative AFM images for bare RC, s-CNC, and d-CNC films exposed to 10 mg·L^{-1} and 500 mg·L^{-1} XG. The scans are 2 x 2 µm with a 20 nm z-scale.

Table S3. Root-mean-square (RMS) roughness and aggregate heights for RC, s-CNC, and d-CNC films before and after exposure to a 500 mg·L^{-1} XG solution.

I. Representative Data for Xyloglucan (XG) Adsorption onto Cellulose Surfaces



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II. Determination of Surface Concentration (Γ) by QCM-D and SPR Data

The surface excess, Γ_{QCM}, was calculated using the Sauerbrey equation (Sauerbrey, G. *Zeitschrift für Physik* **1959**, *155*, 206-222.),

$$\Gamma_{QCM} = -C\left(\frac{\Delta f}{n}\right)$$

where f is the frequency, n is the overtone (n = 5 for this work), and C is the Sauerbrey constant (0.177 mg·s·m^{-2}). This equation was originally derived assuming rigidly attached layers in the gas phase that have the same shear modulus and density as quartz. As the QCM-D is sensitive to changes in density and viscosity of the surrounding medium, the addition of a viscous, floppy film containing associated liquid requires use of modeling (e.g. Voigt or Maxwell models) to obtain explicit Γ_{QCM} values for the adsorbed film. An indication of the viscous nature of an adsorbed layer is provided by changes in dissipation (D),

$$D = \frac{E_{dissipated}}{2\pi E_{stored}}$$

where E_{stored} is the energy stored in the sensor crystal and $E_{dissipated}$ is the energy dissipated by the viscous nature of the surrounding medium. An increase in D x 10^6 greater than 5% of the absolute scaled frequency shift ($\Delta f/n$) signifies that the Sauerbrey equation may be invalid. In this work, only adsorption of XG onto RC surfaces fit this criteria. However, application of the Voigt model (Voinova, M. V.; Jonson, M.; Kasemo, B. *Biosensors and Bioelectronics*. **2002**, *17*, 835-841) resulted in an adjusted ($\Delta f/n$) that was less than the spread of the data. Consequently, the Sauerbrey equation was considered to be a good approximation to determine Γ_{QCM}.

The surface excess, Γ_{SPR}, was calculated using the equation by de Feijter et al. (J. A. De Feijter, J. Benjamins, F. A. Veer, *Biopolymers* **1978**, *17*, 1759),

$$\Gamma_{SPR} = \frac{L(n_a - n_s)}{dn/dc} = \frac{\Delta\theta}{d\theta/dL}\frac{(n_a - n_s)}{dn/dc}$$

where θ_{sp} is the irreversibly bound adsorbate, n_a is the refractive index of the adsorbate, n_s is the refractive index of the solvent, $d\theta/dL$ is the change in surface plasmon angle with thickness as modeled by the Fresnel equations, and dn/dc is the refractive index increment (Table S1).

Table S1. Values used in the de Feijter equation to convert measured SPR data into surface excesses.

Parameter	Value
n_a (BSA)	1.45 [a]
n_s (water)	1.328 [b]
$d\theta/dL$	0.043 deg·nm^{-1} [a]
dn/dc	0.137 cm^3·g^{-1} [c]

[a] Kaya, A.; Du, X.; Liu, Z.; Lu, J. W.; Morris, J. R.; Glasser, W. G.; Heinze, T.; Esker, A. R. *Biomacromolecules* **2009**, *10*, 2451.
[b] Eicher, L. D.; Zwolinski, B. J. *J. Phys. Chem.* **1971**, *75*, 2016.
[c] Determined by differential refractometry. See experimental details of main paper.

III. Adsorption Isotherm Fitting Parameters

Table S2. Freundlich and Langmuir isotherm fitting parameters for XG adsorbed on RC, s-CNC, and d-CNC films as determined from QCM and SPR data.

	K_F (L·mg^{-1})		$1/n_f$		Γ_m (mg·m^{-2})		K_L (L·m^{-2})	
	QCM	SPR	QCM	SPR	QCM	SPR	QCM	SPR
RC	2.01 ± 0.07	0.33 ± 0.02	0.10 ± 0.01	0.14 ± 0.02	-	-	-	-
s-CNC	-	-	-	-	4.8 ± 0.2	2.3 ± 0.2	0.09 ± 0.04	0.07 ± 0.01
d-CNC	3.2 ± 0.1	2.2 ± 0.3	0.19 ± 0.01	0.17 ± 0.03	-	-	-	-

IV. Roughness and Aggregate Heights of Model Surfaces

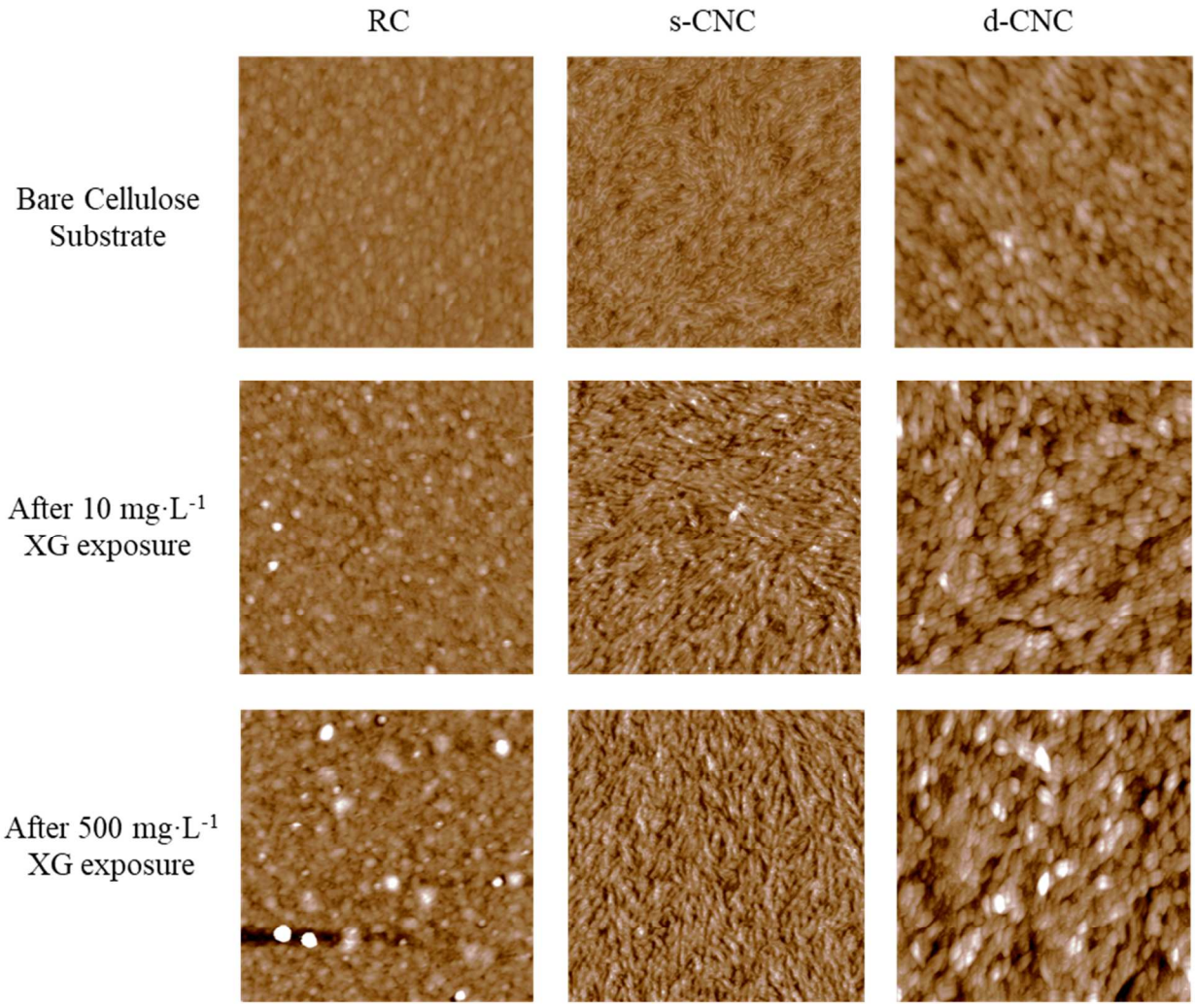

Figure S2. Representative AFM images for bare RC, s-CNC, and d-CNC films exposed to 10 mg·L^{-1} and 500 mg·L^{-1} XG. The scans are 2 x 2 μm with a 20 nm z-scale.

Table S3. Root-mean-square (RMS) roughness and aggregate heights for RC, s-CNC, and d-CNC films before and after exposure to a 500 mg·L^{-1} XG solution.

		RMS Roughness (nm)	Aggregate Height (nm)
RC	Bare	1.56 ± 0.01	9 ± 2
	After XG	3.8 ± 0.9	20 ± 12
s-CNC	Bare	2.3 ± 0.3	-
	After XG	2.3 ± 0.3	-
d-CNC	Bare	3.04 ± 0.04	9 ± 1
	After XG	3.5 ± 0.1	11 ± 2