

Supporting information

Methods

Stagnation Point Adsorption Reflectometry (SPAR) The theory of the method is thoroughly described elsewhere^{1,2} and will only be briefly covered below.

In the SPAR equipment the adsorbent is added in a continuous perpendicular flow to a silica substrate. A linearly polarized laser beam is focused on the stagnation point and is reflected onto a detector where the intensities of the parallel and perpendicular components, I_p and I_s , of the reflected polarized light are registered. The output from the instrument, S , equals the ratio of these two components, I_p/I_s . Adsorption of polyelectrolytes/MFC to the silica substrate changes the refractive index of the surface. This leads to a relative change in the reflected intensities, I_p and I_s , and thus to a change in S . For thin layers, the adsorbed amount, Γ , is proportional to the normalized response in the reflectometer signal, $\Delta S/S_0$, according to equation 1.

$$\Gamma = \frac{1}{A_s} \frac{\Delta S}{S_0} \quad (1)$$

where ΔS is the change in reflectometer signal upon adsorption and S_0 refers to the signal prior to adsorption. A_s is a sensitivity factor dependent on the thickness of the silicon oxide layer, the refractive indices of the silicon, silica, adsorbent and the bulk solvent and the refractive index increment (dn/dc) of the adsorbed polyelectrolytes/MFC. A four-layer optical model was used together with the “Prof. Huygens” software (Dullware, The Netherlands) to determine A_s . The refractive index increment (dn/dc) of the adsorbed polyelectrolyte/MFC was determined by an Optilab DSP interferometric refractometer (Wyatt Technology, Santa Barbara, US). The refractive index increment was found to be $0.22 \text{ cm}^3/\text{g}$ for PEI and 0.14 and $0.12 \text{ cm}^3/\text{g}$ for the cationic and anionic MFC, respectively.

Quartz Crystal Microbalance with Dissipation (QCM-D) The resonance frequency of a quartz crystal, which under ideal conditions is proportional to the mass of the crystal, is continuously monitored. A frequency decrease is detected upon adsorption. For thin, rigidly attached films, the Sauerbrey relationship³ is assumed to be valid:

$$\Delta m = C \frac{\Delta f}{n} \quad (2)$$

The adsorbed mass, Δm , is proportional to the change in resonance frequency upon adsorption, Δf . C is a sensitivity constant equal to 0.177 mg m^{-2} ,⁴ and n is the overtone number. This adsorbed mass contains both the solid amount of adsorbed polymer and the amount of solvent (i.e. water) immobilized by the adsorbed layer. For more loosely or highly viscoelastic adsorbed layers, the film is too soft to fully couple as an oscillator i.e., the upper parts of the adsorbed layer, far away from the surface, do not couple elastically to the oscillation of the sensor. This also means that the most common way to calculate the mass directly from the change in frequency, the Sauerbrey equation, may

underestimate the mass. Hence, the Sauerbrey relationship can be used only as an approximation to convert the observed frequency shift to the adsorbed mass. Therefore, the data were also analyzed using the model of Johannsmann et al.,⁵ who derived the following equation to enable the true sensed mass to be calculated for the viscoelastic layers:

$$\delta\hat{f} \approx -f_0 \frac{1}{\pi\sqrt{\rho_q\mu_q}} \left(f\rho d + \hat{J}(f) \frac{f^3 \rho^2 d^3}{3} \right) \quad (3)$$

where $\delta\hat{f}$ is the shift in the complex frequency, f_0 is the fundamental resonance frequency of the quartz crystal in air, f is the resonance frequency of the crystal in contact with solution, d is the thickness of the film, and $\hat{J}(f)$ is the complex shear compliance. The quantities ρ_q and μ_q are the specific density and elastic shear modulus of quartz, respectively, and ρ is the density of the fluid. Equation 3 can be transformed into a more convenient form using the equivalent mass (\hat{m}^*) defined by

$$\hat{m}^* = -\frac{\sqrt{\rho_q\mu_q}}{2f_0} \frac{\delta'f}{f} \quad (4)$$

which yields

$$\hat{m}^* = m^0 \left(1 + \hat{J}(f) \frac{\rho f^2 d^2}{3} \right) \quad (5)$$

The true sensed mass, m^0 , was calculated under the assumption that $\hat{J}(f)$ is independent of the frequency in the accessible frequency range. A plot of the equivalent mass against the square of the resonance frequency, f^2 , gives the true sensed mass as the intercept. The dissipation factor, D , is defined as

$$D = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}} \quad (6)$$

where E_{stored} is the energy stored in the oscillating system and $E_{\text{dissipated}}$ is the energy dissipated during one oscillation period.⁶ A relationship between the change in dissipation during adsorption and the viscoelastic properties of the adsorbed layer can be found. A thin, rigidly attached film is expected to give a low change in dissipation while a thicker, more water-rich and mobile film is expected to give a large change in dissipation.

X-ray Photoelectron Spectroscopy (XPS)

XPS was used to characterize the chemical composition of the MFC-based multilayer films. The XPS spectra were collected with a Kratos Axis Ultra DLD electron spectrometer (UK) using a monochromated AlK_α source operated at 150 W, with a pass energy of 160 eV for wide spectra and a pass energy of 20 eV for individual

photoelectron lines. The surface potential was stabilized by the spectrometer charge neutralization system. Photoelectrons were collected at a take-off angle of 90° relative to the sample surface and the depth of analysis was ca. 10 nm. The binding energy (BE) scale was referenced to the C 1s line of aliphatic carbon, set at 285.0 eV. The spectra were processed with the Kratos software including experimental values for the atomic sensitivity factors, and peak intensities were determined by integrating the areas under the peaks.

Results

Table S1 shows the atomic surface concentrations of carbon, oxygen, nitrogen and silicon on the films. A clean SiO₂ surface was used as a reference sample for the MFC films. In all the films, the amount of detected substrate material (silicon) was significantly lower than the reference, indicating that the surface was covered by fibrils. A large Si peak (25.4 %) was seen in the case of the 5 bilayer cationic/anionic MFC film. Taking into account that the depth of analysis by XPS is about 10 nm, the large Si peak may be due to either a very thin film or an inhomogeneous film. Only traces of nitrogen (< 0.1%) derived from the cationic MFC was detected. In the case of the PEI/anionic MFC film; carbon, oxygen, and small amounts of nitrogen from the incorporated PEI was detected, but no silicon. This indicates that the surface is fully covered by the PEI/anionic MFC multilayer. The 5 bilayer cationic/anionic MFC multilayer shows a lower carbon and higher oxygen content than expected from the formula for cellulose (C₆H₁₀O₅)_n, whereas the PEI/anionic MFC multilayer shows a higher carbon and lower oxygen content than pure cellulose. The oxygen to carbon ratio (O/C) for 5 bilayers of cationic/anionic MFC and PEI/anionic MFC was calculated to be 0.91 and 0.55, respectively. The theoretical O/C-ratio for cellulose is 0.83. The results indicate that in the case of 5 bilayer cationic/anionic MFC, the XPS most probably also detect oxygen at the silica surface resulting in a slightly higher O/C ratio compared to pure cellulose. Note, that with the XPS technique, it is impossible to distinguish between oxygen in the silicon oxide layer and oxygen in the cellulose. In the case of the PEI/anionic MFC film, the carbons in the PEI molecules most probably contribute to the lower O/C ratio.

Table S1. Atomic surface concentrations on MFC films and their references.

	Surface concentration (atomic %)			
	C	O	Si	N
SiO ₂	7.2	38.5	54.3	
5 bilayer cationic/anionic MFC	39.1	35.5	25.4	
5 bilayer PEI/anionic MFC	61.8	34.1		3.1

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- (4) Edvardsson, M.; Rodahl, M.; Kasemo, B.; Höök, F. *Analytical Chemistry* **2005**, *77*, 4918-4926.
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