Supporting Information

Reversible Swelling of Chitosan and Quaternary Ammonium Modified Chitosan Brush Layers: Effect of pH and Counter Anion Size and Functionality

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Mass of polymer brushes grafted onto QCM crystals

In order to determine the extent of swelling in aqueous media, the initial (dry) thickness of the polymer brush must be determined. This thickness can be determined by measuring the (dry) mass of the polymer brush grafted to the SiO_2-coated QCM crystal which is used for the pH-dependent swelling studies in solution. Samples were prepared by cleaning the SiO_2-coated crystals in piranha solution (for 2 min), rinsing with ultrapure water, drying with N_2, and exposing the substrate to UV-Ozone. This last step removes organic impurities and produces a homogeneous hydroxylated surface (**I** in Figure 1S). We first monitored $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n for the treated QCM sensor under air at 21 °C (**I** in Figure 2S (a)). When $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n were stable, the frequency and dissipation were monitored for 1 min (**I** in Figure 2S (a)). Second, GPTMS was grafted onto SiO_2-coated QCM crystal, CH, CH-Q_{25}, and CH-Q_{50} were grafted onto the GPTMS, and finally the surface was rinsed using acidic solution (pH ~4) (**II** in Figure 1S). The thickness and mass of GPTMS on SiO_2-coated crystals included in values of thickness and mass representing the chitosan brush. During the pH-dependent swelling studies, the mass and thickness of GPTMS layer (0.7 nm by spectroscopic ellipsometry) [1] remains constant and therefore does not impact the final value of percent swelling. After grafting the polymer to GPTMS, the sample was placed in a vacuum to remove moisture. We monitored $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n for the CH-Q_{50} grafted QCM sensor under air at 21 °C (**II** in Figure 2S (a)). When $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n were stable, frequency and dissipation were collected for 1 min (**II** in Figure 2S (a)). These two sets of data were combined using Q-soft (Q-Sense). In this way, the frequency and dissipation changes could be determined in air (i.e., dry) before and after polymer grafting (**I** and **II** in Figure 2S (a)). These polymer-grafted sensors were used for pH-swelling studies. After each swelling study, the polymer grafted QCM sensors were exposed to O_2 plasma for 3 min. to remove the organic layer without changing the silicon oxide coating (**III** in Figure 1S), in order to reconfirm the measurement of the mass in region II of Figure 2S(a). We monitored $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n for the O_2 plasma treated QCM sensor under air at 21 °C (**III** in Figure 2S (a)). When $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n were stable, the data of frequency and dissipation were collected for 1 min (**III** in Figure 2S (a)). These two sets of data were also combined using Q-soft (Q-Sense) and showed frequency change and dissipation change depending on mass change under air before and after O_2 plasma (**II** and **III** in Figure 2S (a)).

Figure 2S (a) shows the QCM-D results for the SiO_2-coated QCM sensor (**I**), CH-Q_{50} grafted onto the GPTMS-derivatized SiO_2-coated QCM sensor (**II**), and the O_2 plasma treated QCM sensor (**III**). For the three modes (n = 3, 5, 7), the values of f_n/n for each crystal superimposed and ΔD_n exhibited its lowest value, ~0. These results suggest that the each layer behaves like an elastic solid. Between regions I and II, $\Delta f_n/n$ ($n = 3, 5, 7$) is found to decrease by - 25.7 ± 0.3 Hz due to mass increase resulting from the grafting of CH-Q_{50} onto the QCM sensor. After removing CH-Q_{50} and GPTMS using the O_2 plasma, $\Delta f_n/n$ ($n = 3, 5, 7$) returns to its original value prior to surface modification of the QCM sensor (Figure 2(a)). The physical properties (mass deposited, grafting density, and thickness) of the elastic CH-Q_{50} layer were calculated using the Sauerbrey equation, $\Delta f_n/n$ ($n = 3, 5, 7$), chitosan molecular weight, and chitosan density (cg10: Mw = 60 kDa, density = 0.54 g/cm^3).[1] Figure 2S (b) shows calculated thickness corresponding to the initial surface (**I**), CH-Q_{50} /GPTMS modified surface (**II**), and surface after removing the organic layer (**III**). As a result, the mass density of CH-Q_{50}, grafting density, and thickness are 456 ± 5 ng/cm^2, 0.046 ± 0.001 chains/nm^2, and 8.4 ± 0.1 nm, respectively. The self-consistent behavior of the QCM crystal, before and after modification with the polymer brush, and after removing the polymer brush ensures that the interpretation of changes in frequency and dissipation are reliable.

References

[1] H. Lee, D. M. Eckmann, D. Lee, N. J. Hickok and R. J. Composto, Langmuir 2011, **27**, 12458

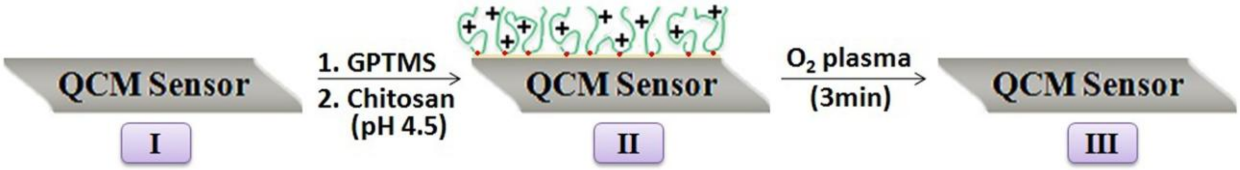

Figure 1S. Experimental scheme to accurately determine the mass of the grafted chitosans (CH, CH-Q_{25}, and CH-Q_{50}) on SiO_2-coated QCM sensors.

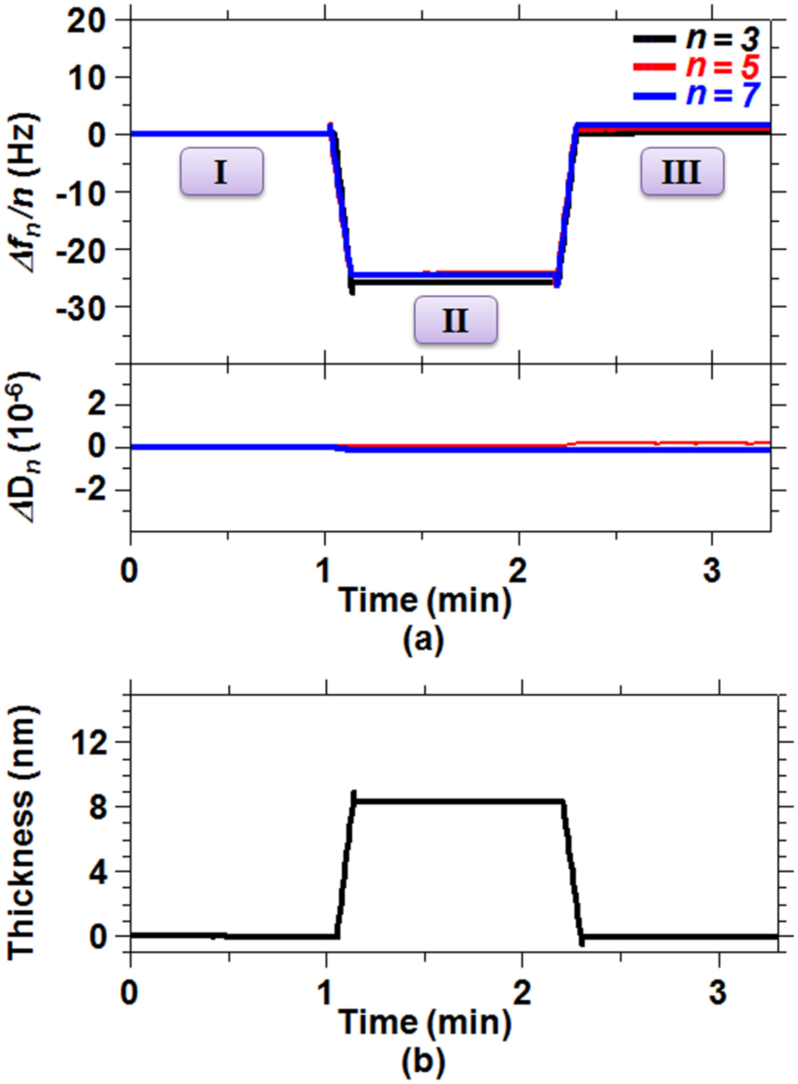

Figure 2S. (a) Traces of $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n of cleaned SiO_2-coated QCM sensor (**I**), CH-Q_{50} grafted onto GPTMS-derivatized SiO_2-coated QCM sensor (**II**), O_2 plasma treated QCM sensor (**III**) under air at 21 °C, respectively. The data from regions **I**, **II**, and **III** were combined using Q-soft (Q-Sense). (b) Dry thickness of CH-Q_{50} in air was determined using chitosan density (0.54 g/cm^3) and the dry masses of the grafted polymers calculated using the Sauerbrey equation.

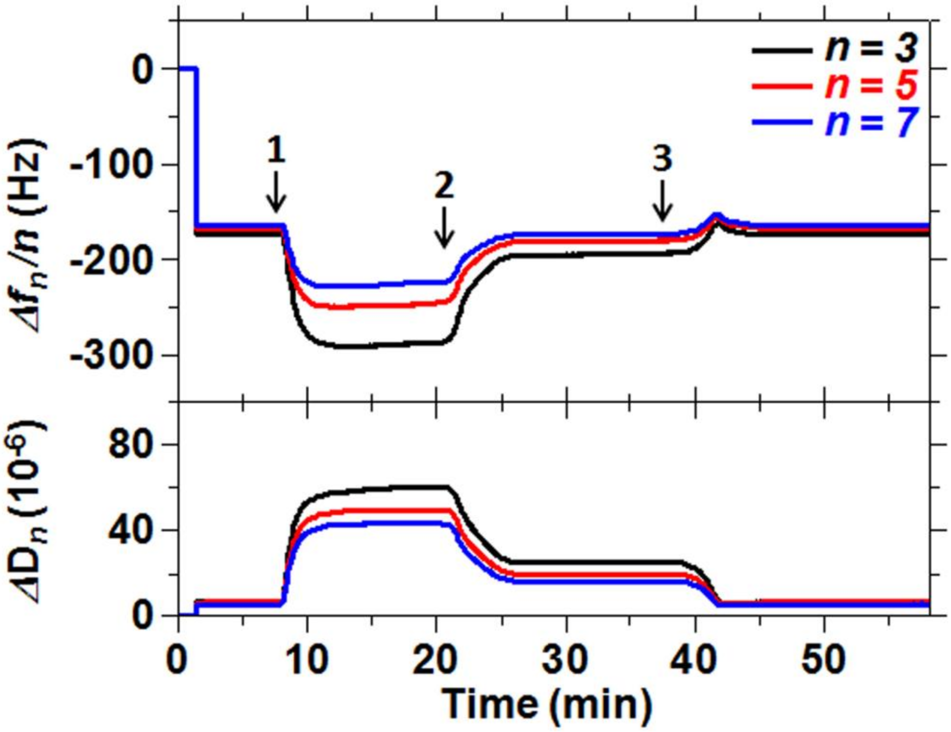

Figure 3S. Traces of $\Delta f_n/n$ (n = 3, 5, 7) and ΔD_n of the CH-Q$_{25}$ layer as a function of sequential changes in solution pH. Arrows 1, 2, and 3 represent the change from pH 7.06 to pH 4.05 (with acetate anions), pH 4.05 to pH 4.08 (with citrate anions), and pH 4.08 to pH 7.06, respectively. Thus the layer returns to its original properties after changing the pH and anion type in the medium.

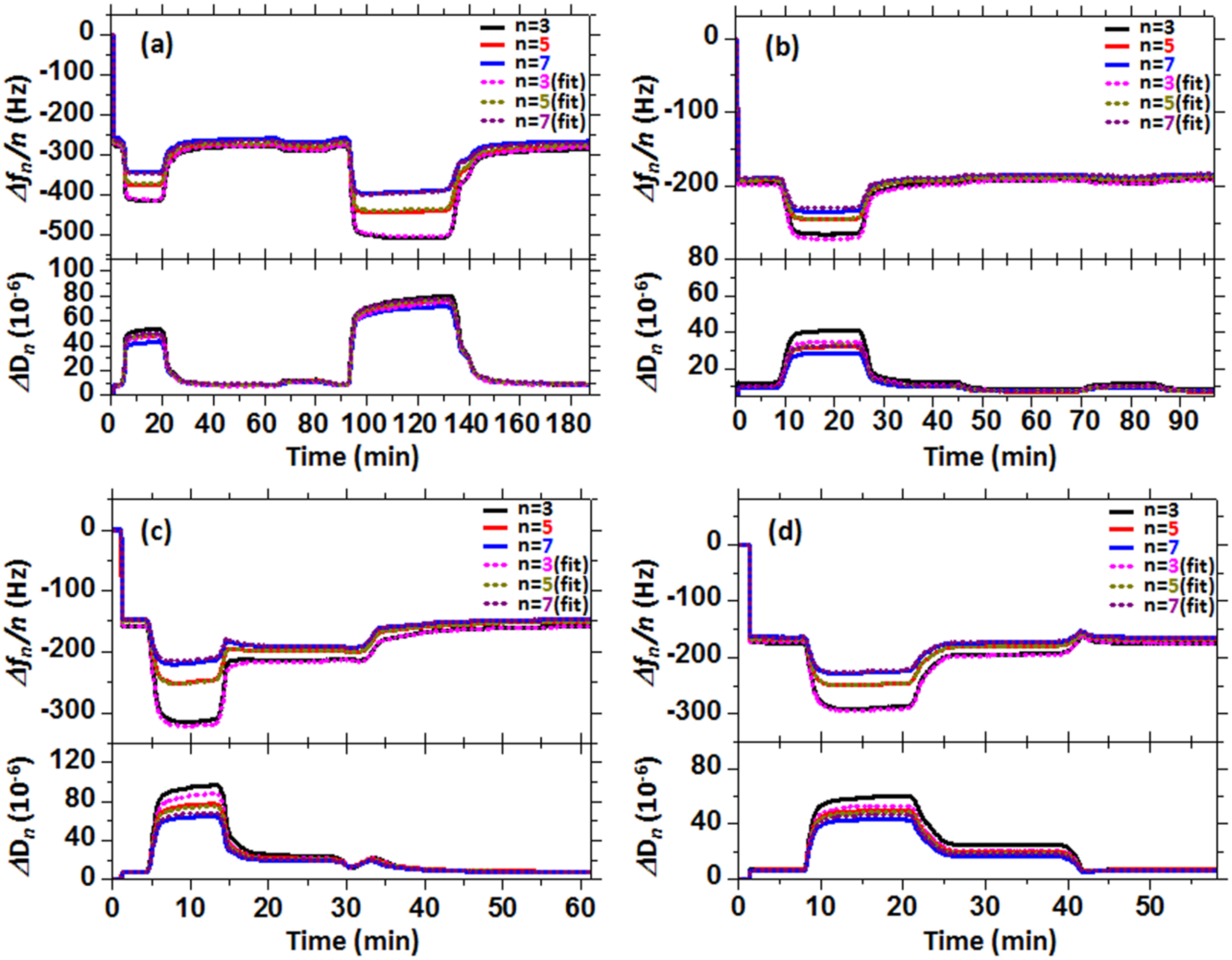

Figure 4S. Simulated and experimental curves (a), (b), (c), and (d) for $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n corresponding to Figure 3(a), Figure 4(a), Figure 6, and Figure 3S, respectively. For the four studies, the agreement between experiment and fit for all three vibration modes is excellent.

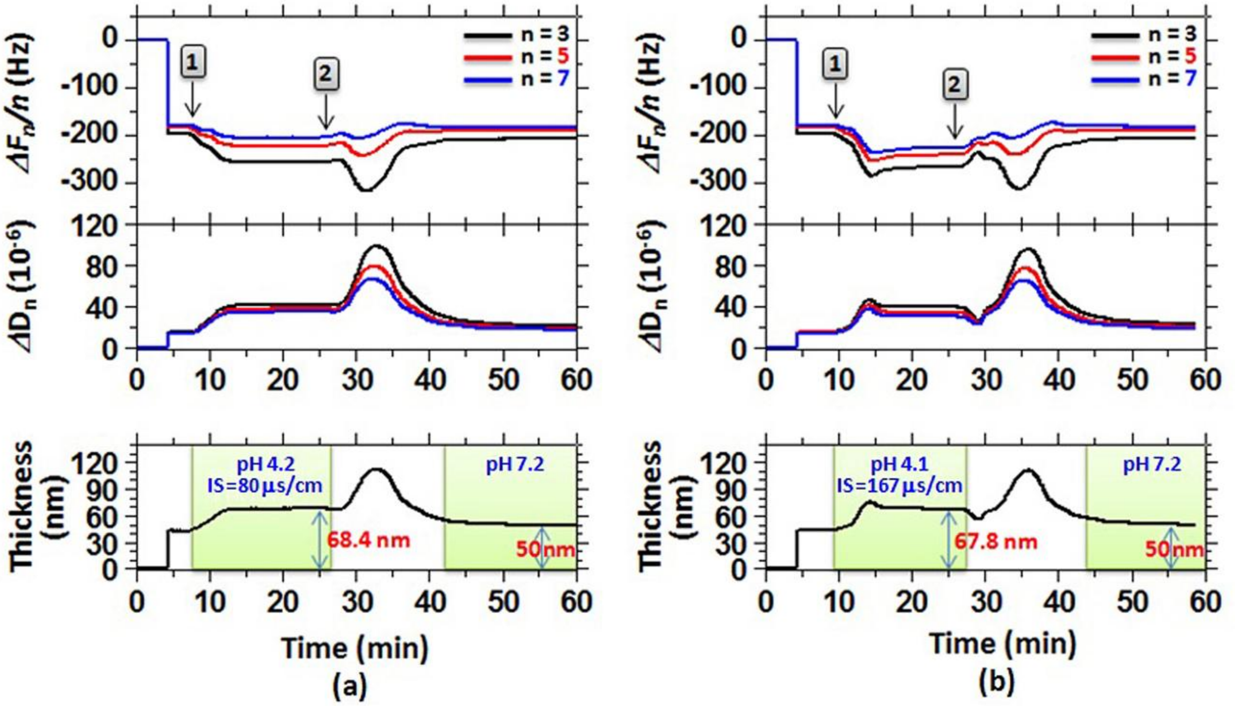

Figure 5S. (a) Traces of $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n for a CH layer as a function of sequential changes in solution pH. Thicknesses are determined from the best fit of the QCM-D data using the viscoelastic model. Arrows 1 and 2 represent the change from pH 7.20 (Ionic strength = 12.6 µs/cm) to pH 4.20 (Ionic strength = 80 µs/cm), and pH 4.20 to pH 7.20, respectively. (b) Traces of $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n for a CH layer as a function of sequential changes in solution pH. Thicknesses are determined from the best fit of the QCM-D data with the viscoelastic model. Arrows 1 and 2 denotes the change from pH 7.20 (Ionic strength = 12.6 µs/cm) to pH 4.10 (Ionic strength = 167 µs/cm), and pH 4.10 to pH 7.20, respectively. Comparison of (a) and (b) shows that the thickness changes from 50 nm to about 68 nm upon decreasing the pH. Thus the same swelling behavior is observed at the two ionic strengths investigated. The thickness returns to original value when the solution pH returns to 7.20.