Real-Time Characterization of Polymer Film Degradation with Quartz Crystal Microbalance with Dissipation Monitoring

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ABSTRACT

There is a growing need for new technologies to quantitatively measure the surface properties of material interfaces. One technique in particular, the Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D), fulfills the need for monitoring real-time dynamic adsorption and desorption phenomena. Capable of operating in both gas and liquid environments in real-time, QCM-D provides a powerful approach to analyze the *in situ* thickness, structural, and viscoelastic properties of both film formation and reactions within the film itself. This presentation will focus on the application of QCM-D to monitoring the light induced degradation of a polymer film with unique photo-physical properties. We found that light of differing wavelengths and intensity exhibited a response from the QCM-D sensor alone and that the response could be accounted for to negate signal changes as a result of light irradiation. This allowed us to monitor the extent of degradation of the polymer film poly (2,5-methoxy-propyloxy sulfonate phenylene vinylene) (MPS-PPV) by UV light. Based on numerous control experiments we were able to determine fundamental light intensity / QCM-D signal correlations that led us to believe there may be potential for the QCM-D sensor to act as a light transducer.

Keywords: QCM-D, polymers, polyelectrolyte multilayers, degradation.

INTRODUCTION

Polyelectrolyte multilayers (PEMs) have received much attention over the last two decades since their initial development and characterization by Decher.[1-3] The interest has largely stemmed from the wide variety of potential applications ranging from optical to biomedical. The majority of research on PEMs involves ideal controlled environments in the laboratory. If the coatings are to be commercialized and used in real world applications, i.e. solar cells, then a better understanding of how the coatings will react to ambient conditions is necessary.

In this paper we demonstrate the procedure for testing the response of PEMs to UV light. Specifically, the photoinduced degradation effects of poly (2,5-methoxy-propyloxy sulfonate phenylene vinylene) (MPS-PPV) are demonstrated. Here we take advantage of the sensitivity and stability of a commercially available quartz crystal microbalance with dissipation (QCM-D) instrument to monitor the decrease in mass and thickness of a PEM induced by UV light. Additionally, light intensity / QCM-D signal changes were measured as part of control experiments and found to indicate the potential for QCM-D sensors to act as light transducers.

QCM-D BACKGROUND

Ever since the work of Sauerbrey in 1959[4] quartz crystal microbalances (QCMs) have been used to monitor the uptake of mass in vacuum. Commonly, QCMs are used in semiconductor metal plating applications to measure the thickness of deposited thin films in real-time. More recently, application of QCMs to liquid mediums has opened up numerous possibilities of applying this technique to the fields of nanotechnology, biotechnology, biology, drug delivery, etc., where real-time, *in situ* analysis of interactions of nanoscale molecules/particles at various surfaces, in the liquid medium is of critical importance.

A QCM consists of a thin quartz disc sandwiched between a pair of electrodes. Due to the piezoelectric properties of quartz, these crystals can be excited to oscillate at their resonance frequency (f) by applying an AC voltage across the electrodes. In the event of adsorption onto the surface of an oscillating quartz crystal, the resonant frequency will decrease. The resonance frequency of the crystal depends on the total oscillating mass, including water coupled to the oscillation. For a thin and rigid film the decrease in frequency is linearly proportional to the adsorbed mass which is defined by the Sauerbrey relation.[4]

$$\Delta m = -\frac{C \cdot \Delta f}{n}$$

$C = 17.7$ ng Hz^{-1} cm^{-2}
$n = 1,3,5$, etc. is the overtone number.

In many situations the adsorbed film is not rigid and the Sauerbrey relation becomes invalid. By measuring the energy loss of the oscillator or dissipation (D) it can be possible to more fully characterize floppy or viscoelastic films. The dissipation parameter in combination with

several frequencies and appropriate models allow determining whether the adsorbed film is rigid or viscoelastic (soft). In contrast, conventional QCMs only measure changes in frequency and fail to fully characterize a soft film.

With QCM-D, simultaneous measurement of resonance frequency change (Δf) and energy dissipation change (ΔD) is performed by periodically switching off the driving power of oscillation of the sensor crystal and recording the decay of damped oscillation as the adsorption and/or structural changes take place at the sensor crystal surface (Figure 1). While change in frequency provides information about mass changes, changes in dissipation (D) provide structural information about the viscoelastic properties of adsorbed films in real time.
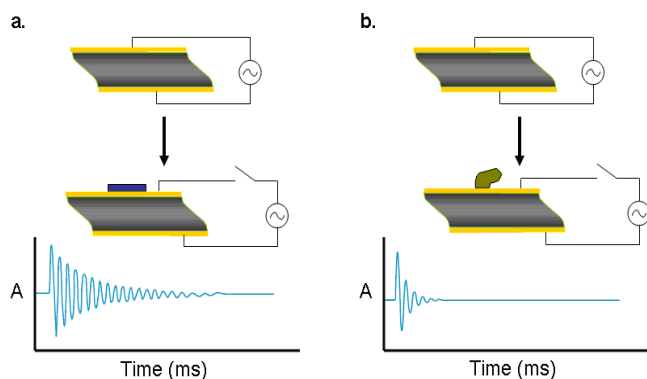
Figure 1. Schematic depicting the viscoelastic differences between (a) a rigid material and (b) a soft viscoelastic material. In each case (a and b), changes in frequency (change in mass) and dissipation (change in viscoelasticity) are monitored simultaneously.

Figure 2 represents a typical frequency change (Δf) and energy dissipation change (ΔD) vs time plot for protein-protein interactions. By measuring at multiple frequencies and applying a viscoelastic model (the so called Voigt model), the adsorbed film can be characterized.
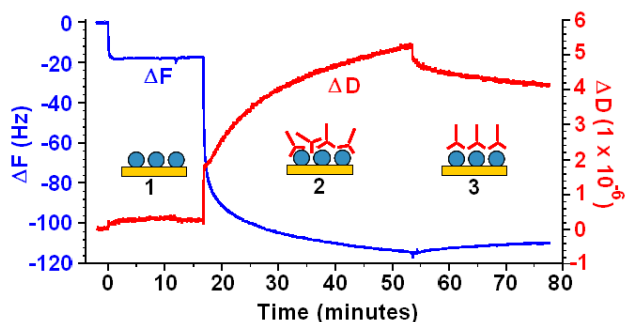
Figure 2. Frequency change (Δf) and dissipation change (ΔD) vs time plot for human serum albumin (HSA) and an antibody for HSA reaction on a gold surface. Step 1: adsorption of HSA on to the crystals surface, Step 2: reaction of antibody with the adsorbed HSA molecules, step 3 rinsing of loosely bound molecules and reorganization.[5]

QCM-D offers flexibility in selection of different surfaces which enables study of nanoscale interactions/reactions on a wide variety of materials.

EXPERIMENTAL

Materials:

Polyethylenimine (PEI) (Aldrich, CAS 9002-98-6, avg. MW = 25,000 g mol^{-1}). Poly(2,5-methoxy-propyloxy sulfonate phenylene vinylene) (MPS-PPV) (Aldrich, CAS 138184-36-8). Silicon dioxide - coated 5-MHz quartz sensor crystals were used and cleaned using the following protocol: UV/ozone treatment for 10 minutes followed by cleaning in a 2% Hellmanex solution (Hellma Co.) for 30 minutes and rinsing with DI water and thereafter UV/ozone treatment for another 10 minutes.

Polymer solutions were prepared at 10 mM using ultrapure water resistivity > 18 MΩ/cm (Milli-Q-plus system, Millipore, Bedford, MA).

Procedure:

Polyelectrolyte bilayers are created by dry casting 50 μl each of an anionic layer of 10 mM anion, polyethylenimine (PEI) followed by a cationic layer of .4 mM poly(2,5-methoxy-propyloxy sulfonate phenylene vinylene) (MPS-PPV). The PEI layer is pipetted onto the surface of a SiO_2 crystal having undergone the standard cleaning procedure, and allowed to evaporate in vacuum. In order to preserve the photo- and thermo-sensitive structure of MPS-PPV, the cationic layer is evaporated in a dark, refrigerated chamber.

After complete evaporation of both polymers, a Stokes Ellipsometer (Gaertner Scientific, Skokie, Illinois) was used to determine the initial thickness of the PEI/MPS-PPV bilayer. The crystal sensor is then inserted into the QCM Open Module (Q-Sense, Gothenberg, Sweden) and the module is placed in the QCM-D (E4, Q-Sense, Gothenberg, Sweden). Cell temperature is set at 19 °C and a UV Lamp (UVG-11, UVP, Upland, California) covered the opening in the open module. Once a stable baseline is achieved, the UV lamp is switched on. Photodegradation occurs, and once a stable baseline is again reached, the lamp is switched off, until arriving at a final baseline. The UV irradiation causes a surface heating on the crystal surface, inducing an increase in frequency in addition to the increase caused by the photodegradation. This surface heating related frequency increase was repeatable and constant for the same light source, therefore, the total frequency increase due to photodegradation is reflected by the final Δ*f* after the light source is switched off.

After irradiation, ellipsometric measurements were taken again to find the films change in thickness. Δf and ΔD plots were recorded at 5 overtones (3rd 5th 7th 9th and 11th) and fundamental frequency (5 MHz) of crystal sensor. For clarity, data for only a single overtone is shown.

RESULTS AND DISCUSSION

Control Experiments to Measure Effects of UV Light:

The typical QCM-D response to light is shown in Figure 3. A clean bare SiO_2 coated sensor is irradiated with a broad spectrum UV light at 19 ^{o}C from ~ 4 cm away giving ~ 6 Hz frequency shift and little to no dissipation change < 0.1. The change in frequency is likely due to light being absorbed by the electrode causing localized heating (perpendicular to the electrode) of the crystal. This temperature gradient can cause stress in the quartz. Since most quartz crystals have a strong frequency response to stress, the frequency changes are likely due to this induced stress.

The effect of temperature was investigated by measuring the response at 50 ^{o}C. The same magnitude response was found indicating the light induced frequency change is not affected by temperature (at least in the range 19 - 50 ^{o}C). Ambient room light was found to not affect the readings since the same results were found with the laboratory lights both on and off.
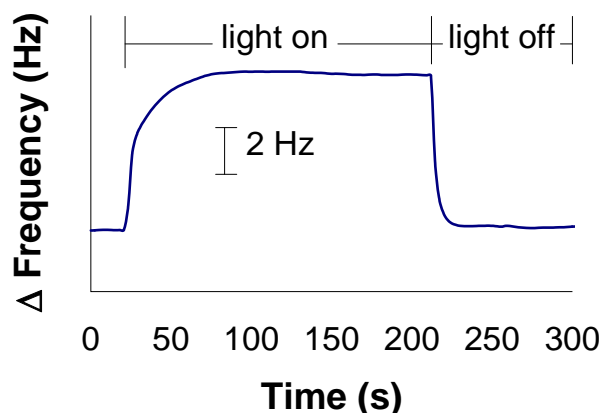
Figure 3. Typical frequency response (3rd harmonic) to light irradiation. This example specifically shows a SiO_2 sensor response to broad spectrum UV light at 50 ^{o}C.

In order to determine the effect of light intensity on the frequency response the source was progressively moved further away from the QCM-D sensor in increments of 2 cm. The distance dependence of the light source to the signal change is shown in Figure 4 and indicates there is a correlation between light intensity and frequency change. This stands to reason since a higher power light source should cause more light to be adsorbed and thus more stress to be imparted onto the quartz crystal.

In general, the intensity of a point light source (I) can be related to distance (r) from the light source by $I = 1/r^2$ using the inverse square law for light intensity. The distance from the UV broad spectrum lamp to the sensor was measured using a ruler and the source was positioned using a ring stand and clamp. When an inverse second order equation is fit to the data an R^2 of 0.98 is found.
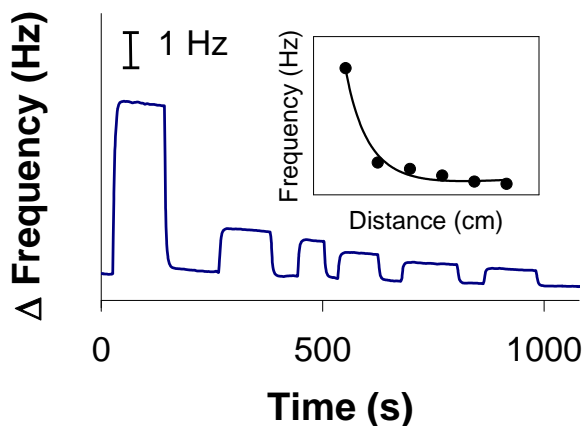
Figure 4. Frequency response (3rd harmonic) as a function of source distance. The source was positioned at its closest point 4 cm away from the sensor and moved progressively away in 2 cm increments. Inset shows the inverse second order fit.

Polyelectrolyte Multilayer Degradation by UV light:

After several control experiments the effect of UV light on PEMs was tested. The raw frequency changes as a result of UV light irradiation at a distance of 4 cm are shown in Figure 5. Initially, after the light is turned on the frequency response increases slowly (compared to Figure 3) indicating that the changes are due to polymer effects and not light induced sensor effects. Additionally, after the light is turned off the frequency change levels off above zero (unlike Figure 3 that returns to zero) indicating that the light induced an irreversible change in the polymer film.
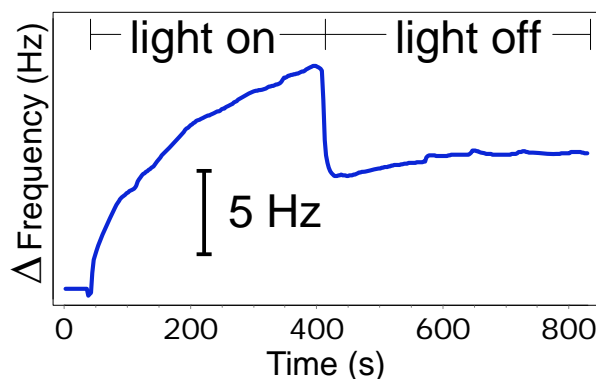

Figure 5. Frequency change (5th harmonic) of MPS-PPV as a result of UV light exposure.

The data was modeled using the Sauerbrey equation and the PEM was assumed to have a density of 1.3 g/cm^3 based on a previous study.[6] The average thickness change of three trials (after UV exposure) was found to be 1.7 +/- 0.8 nm. The large standard deviation is likely due to the complexity in polymer film formation. The thickness as measured by QCM-D agrees well with the ellipsometric

thickness (1.6 nm). Further study to elucidate the photo induced chemical changes in the PEM is currently under way.

Bare Sensor Intensity and Wavelength Dependence:

The distance dependence found in Figure 4 suggested the magnitude of the frequency response was dependent on the intensity of light. This led us to investigate the effect of wavelength using red (633 nm) and green (514 nm) lasers as well as more details regarding intensity effects using neutral density filters and a power meter. Figure 5 shows the wavelength and intensity dependence for the 3rd harmonic. The 633 nm laser (with a maximum laser power of 1.3 mW) induced a ~4 Hz shift. The intensity was varied from 100 % to 12.5 % transmittance and shows a linear dependence.
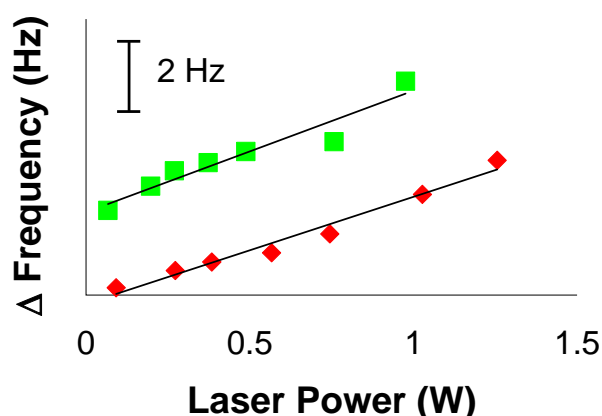
Figure 5. Intensity and wavelength dependence of the frequency response (3rd harmonic) for a 514 nm laser (green squares) and 633 nm laser (red diamonds).

The different responses of the two different wavelengths are anticipated since the magnitude of the frequency response is directly related to how much light is adsorbed by the electrode. The linear fits gave similar slopes for the two different wavelengths, but dramatically different intercepts indicating the 514 nm wavelength must be more strongly adsorbed by the SiO_2 electrode.

CONCLUSION

Photoinduced changes in polyelectrolyte multilayers were measured using a commercial QCM-D instrument. Control experiments showed that UV light itself caused significant frequency responses on bare SiO_2 sensors and that these responses were dependant on light intensity. Thickness changes of the PEMs were found to be on the order of 1.7 +/- 0.8 nm by QCM-D and corroborated by ellipsometry. The QCM-D sensors themselves were found to give linear frequency responses from 514 and 633 nm lasers indicating that the sensors could be used as light transducers.

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