

LETTERS

In Situ Investigations of Polyelectrolyte Film Formation by Second Harmonic Generation

Richard A. McAloney and M. Cynthia Goh*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6

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Multilayer films of polyelectrolytes can be prepared by sequential immersion of a charged silica surface into cationic and anionic polyelectrolyte solutions. The formation of such films was investigated using second harmonic generation (SHG), yielding real time information about the in situ adsorption process of each layer within the multilayer film. The SHG results indicate the existence of a fast process (<10 s) that can be ascribed to the initial polymer adsorption to the surface, followed by a slower relaxation due to a change in polyelectrolyte conformation at the surface. The time scale for the reconfiguration varies with the polyelectrolyte.

Introduction

The controlled production of organized thin films, both mono- and multilayer, and their possible importance in the creation of novel materials, has been discussed since the time of Langmuir.¹ Iler² first described the formation of multilayer assemblies by spontaneous adsorption of alternating layers of positively and negatively charged colloids on a charged surface. In the past few years, driven in large measure by the interest in devices, sensors, specialized coatings, etc., there has been a resurgence of interest in this "dipping" technique.³ This relatively simple, yet effective, procedure has been used for the layer-by-layer deposition of a variety of materials, including biological,^{4–11} inorganic,^{12,13} dyes/polymer dyes,^{14–17} conjugated polymers,^{18–24} and particles,^{25–30} producing supramolecular assemblies with interesting properties and potential for numerous applications. Nevertheless, the adsorption process that is key to the production of these layers merits further scrutiny, since there is limited information, in part due to the difficulty of tracking the interfacial process as each layer is grown. Quartz crystal microbalance¹⁷ and surface plasmon resonance scattering¹³

measurements have been reported, but further work remains to be performed to elucidate the kinetics of the deposition.

In this paper, we examine the utility of second harmonic generation (SHG) for such a task. SHG is a nonlinear optical technique that has interfacial specificity, and has been utilized in studies of liquid/solid interfaces.^{31–35} We investigate the sequential adsorption of anionic and cationic polyelectrolytes on a charged silica surface by monitoring the time dependence of the SHG signal.

Experimental Procedure

Materials. The polycation PDDA (polydiallyldimethylammonium chloride; MW 400 000 to 500 000, Aldrich Chemical Co.), and polyanion PSS (polystyrene sulfonic acid, sodium salt; average MW = 500 000, Polysciences) were used as received to prepare 1 mg mL⁻¹ aqueous solutions, using purified water (resistivity >18 M Ω /cm; pH ~ 5.6). The substrate used was a fused silica prism (Edmund Scientific) cleaned in hot nitric acid (concentrated) for a minimum of 5 h.

Film Preparation. The prism was mounted on a Teflon dish such that it was in contact with the solution. The dish was configured to allow the flow of the polyelectrolyte solution, or

* Author to whom correspondence should be addressed. Phone/Fax number: 416-978-6254. E-mail: cgoth@alchemy.chem.utoronto.ca.

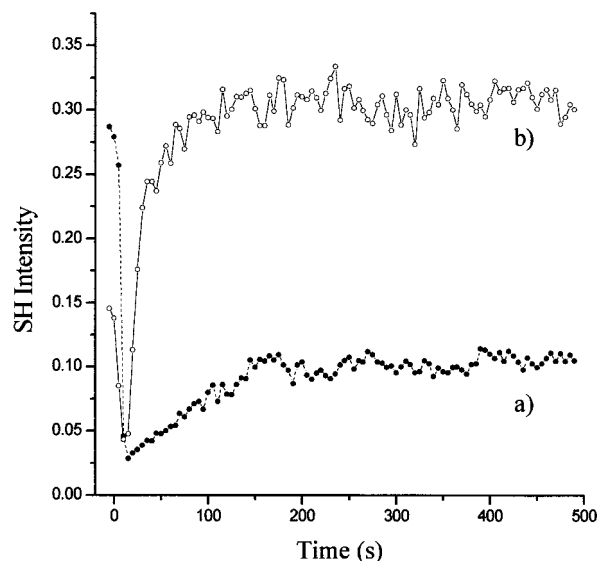


Figure 1. The SH intensity (arbitrary units) as a function of time after deposition of (a) the first PDDA layer, and (b) the first PSS layer.

of the rinse water. A magnetic stir bar was used to ensure rapid delivery of the polyelectrolytes to the surface. Depositions were carried out by introducing one solution, allowing some time for relaxation, rinsing with purified water, then introducing the other solution. This procedure was repeated to produce multiple layers.

Instrumentation. The output of a frequency-doubled Nd:YAG laser (~ 2 mJ/pulse, 50 ps, 532 nm, 10 Hz repetition rate) was gently focused ~ 10 cm before the prism face using a 50 cm focal-length lens. The incident beam on the prism was set at 68° from the normal, for total internal reflection at the prism/solution interface. SH light generated at the interface was detected by a cooled PMT, and normalized to a reference signal produced by doubling the 532 nm light in a KDP crystal. The signals were collected with a boxcar and averaged over 50 laser pulses, resulting in a time resolution of 5 s.

Results and Discussions

SHG is a process that is symmetry-forbidden in isotropic media, such as bulk water and glass. Changes in the SH signal in this experiment are thus indicative of phenomena that occur at the glass/aqueous interface, where the symmetry is broken. When the cationic polyelectrolyte PDDA is introduced into the flow cell, the SH signal changes with time (Figure 1a). At $t = 0$, the signal corresponds to the silica/water (pH 5.6) interface. After PDDA addition, the SH intensity decreased rapidly, reaching a minimum in less than 10 s. The signal then increased to a plateau in ~ 150 s, the magnitude of which is smaller than that from the bare silica/water interface.

After rinsing the PDDA-coated silica with water, the anionic PSS is introduced. A behavior similar to that of the previous layer was observed (Figure 1b). The SH signal rapidly decreased (in < 10 s), then rose sharply for ~ 20 s, and reached a plateau in < 100 s. The plateau, however, is at a higher value than for PDDA.

This trend in the time dependence of the SH signal is reproduced for subsequent adsorption cycles (Figure 2) for the 10 bilayers we studied, indicating a constancy in the dynamics of the adsorption.

To better understand the changes that occur at the interface during deposition, the source of the SH signal has to be examined. SHG from charged aqueous interfaces has been

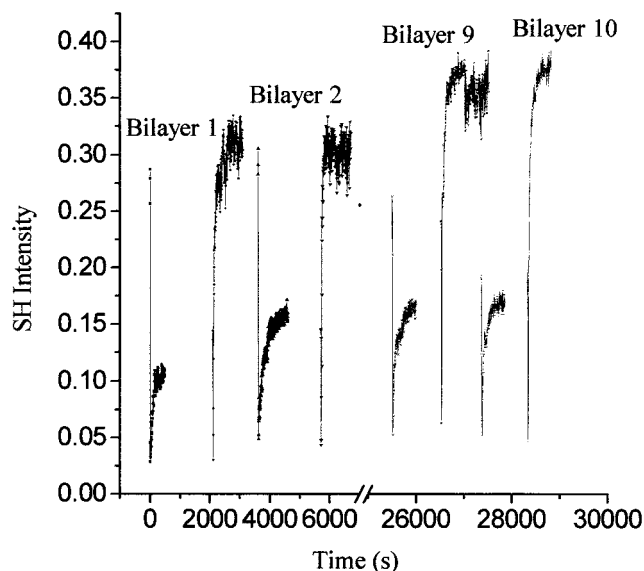


Figure 2. The SH intensity (arbitrary units) as a function of time for the sequential addition of PDDA and PSS in the formation of 10 bilayers. The curves for bilayers 3 to 8 are similar (not shown).

considered in depth by Eisenthal and co-workers,^{36,37} and we follow their exposition. All molecular species at an interface that have a nonzero second-order hyperpolarizability, $\alpha^{(2)}$, and a net dipolar orientation, which leads to a nonzero surface susceptibility $\chi^{(2)}$, contributes to the SH signal. However, in the presence of charges, an additional term due to the surface potential arises, which involves the 3rd-order surface susceptibility, $\chi^{(3)}$. Hence, the polarization, $P_{2\omega}$, which generates the SH signal, has two parts:³⁷

$$P_{2\omega} = \sum_i \chi_i^{(2)} E_\omega E_\omega + \sum_i \sum_j \chi_{ij}^{(3)} E_\omega E_\omega \Psi(0) \quad (1)$$

where E_ω is the incident electric field, and the sum is over all the different species. Thus, in our experiment, the SH signal may have contributions from the silica surface, the polyelectrolyte, the water, and the counterions. We will argue that the contribution from water through the third-order susceptibility dominates the signal.

The hyperpolarizability is frequency-dependent, and if the molecules involved have a net dipolar orientation, resonance-enhancement of the SH signal is expected. In fact, one of the interests in these multilayer films is their potential application to frequency doubling. We chose PSS as the polyanion precisely because it has a (weak) two-photon resonance with our laser, and is thus expected to produce an enhanced SH signal if there is a net alignment of the chromophore. Furthermore, this signal should increase as additional layers of PSS are deposited; the UV-vis absorption spectrum increases linearly with the number of layers (not shown). While indeed the SH signal is reasonably large, the dependence on the number of layers is very weak, if any (Figure 2). Furthermore, the PSS and PDDA signals are not much different, even if PDDA is not close to resonance with the pump laser.

The observations indicate that the benzene sulfonate groups of the PSS have no net dipolar orientation within the deposited film, and that the bulk of the SH signal cannot be ascribed to the polyelectrolytes. The main contribution to the signal thus comes from the water molecules near the interface, and within the polyelectrolyte film, which are oriented by the net charge. In studies of the silica/water interface, Ong et al.³⁷ observed a large enhancement in the SH signal at high pH. They showed

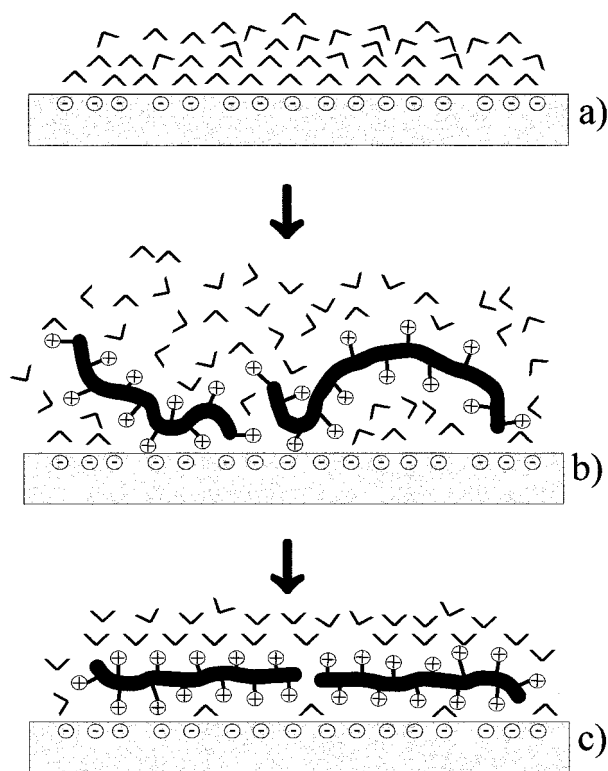


Figure 3. Schematic representation of the distribution of water molecules (Δ) at different times of the polyelectrolyte adsorption. (a) Initially, water molecules are ordered due to the charge on the silica surface. (b) The polyelectrolyte adsorbs, disrupting the order. (c) The polyelectrolyte reconfigures, resulting in the alignment of water molecules in the opposite direction.

that this effect has its origin in the $\chi^{(3)}$ term arising from the alignment of water by the net surface potential. For silica at high pH, ionization of the surface silanol groups produces this effect, while in our studies, the charge of the polyelectrolyte does likewise. Ong et al.³⁷ tested their interpretation by changing the salt concentration, which affects the degree of orientation of the water molecules. In our studies, the salt concentration dependence is more complicated, since the structure and thickness of the adsorbed polyelectrolyte layer, which also has trapped water molecules, will be altered. We thus conducted all measurements at low salt concentrations, where the polyelectrolyte molecules are expected to lay flat against the surface, mimicking the silica/water interface, and simplifying the interpretation of the SH signal.

The time dependence of the signal after deposition of a layer thus reflects changes in the degree of orientation of water molecules near the interface (Figure 3). Initially, water molecules have a net orientation caused by the negatively charged silica. When the polycation PDDA is introduced, they quickly adsorb to the silica, disrupting the ordered water layers, and reducing the SH signal. After adsorption, the PDDA undergoes further conformational relaxation in order to maximize its interaction with the surface. The nearby water molecules experience a potential due to the charges on the PDDA, resulting in some order, and increasing the SH signal. At equilibrium, the PDDA film presents a net positively charged layer, causing a net dipolar orientation of the water molecules opposite to that initially imposed by the negatively charged silica.

Introduction of the polyanionic PSS produces a similar sequence of results, except that the water dipoles orient opposite, pointing in the same direction as those for the original silica surface. This may account for the difference in the equilibrium

SH signals for PSS and PDDA layers. The higher PSS signal may in part be due to a larger $\chi^{(2)}$, but there may also be a contribution from the residual water molecules close to the silica surface that were not displaced by the first layer of PDDA. Any such residual water would have a dipolar orientation pointing in the same direction as those aligned by the anionic PSS, which adds to the SH signal, but opposite to those aligned by the cationic PDDA, which produces cancellation.

The initial adsorption occurs within a few seconds, and is presumably limited by diffusion and the experimental geometry. A subsequent reconfiguration takes ~ 100 s. We can compare these results with the studies of Ariga et al.¹⁷ on the in situ PDDA adsorption using a quartz crystal microbalance (QCM). Depending on the anionic layer used, they observed a plateau in the QCM within 30 to 300 s. This corresponds to the slow time scale of our measurements, which we attributed to the relaxation of the layer, and not to the initial adsorption of the polymer. QCM measurement conducted in solution is sensitive to changes in the viscoelastic properties of the interface,^{38,39} and it is likely that the time scale they obtained reflects not the initial adsorption but the total relaxation process of the adsorbed polymer.

Finally, we note that up to 10 bilayers, the magnitude of the SH signal at equilibrium remains about constant, indicating that the degree of order of the water molecules remain constant from bilayer to bilayer. This means that the net surface charge is the same for, say, the second and the ninth PSS layer, implying that one can build a huge number of layers. This is in fact one of the fascinating aspects of these materials.^{14–16,28}

Summary and Conclusions

We have shown that SHG can be used to monitor the in situ adsorption of polyelectrolytes to a silica substrate. The major source of the SH signal is the ordered water layer, oriented by charges at the polyelectrolyte/solution interface. While we cannot monitor the polyelectrolytes directly, the changes in the water ordering provides information about the time course of the deposition, which appear to proceed in two steps: (1) a relatively fast initial adsorption (≤ 10 s) of the polyelectrolyte; and (2) a relatively slow reconfiguration of the adsorbed layer. We are seeking to further understand these dynamics, and further work with SHG to enable the extraction of surface potentials^{36,37} is being pursued.

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