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Atomic force microscope characterization of poly(ethyleneimine)/poly(ethylene-*co*-maleic acid) and poly(ethyleneimine)/poly(styrene sulfonate) multilayers

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Abstract

We report on an atomic force microscopy study of polyelectrolyte films of poly(ethyleneimine) (PEI), poly(ethylene-*co*-maleic acid) (PMAE) and poly(styrene sulfonic acid) sodium salt (PSS) deposited by the layer-by-layer electrostatic technique. The organic thin films were prepared either following self-assembly in a beaker or in a cell with a continuous flow of the polyelectrolyte solutions. Multilayer structures based on PEI/PMAE bilayers are shown to possess much rougher surfaces than those built-up using PEI/PSS bilayers. This is attributed to the strong polyelectrolyte character of PSS. The deposition method is also shown to influence the morphology of the deposited film. Generally, layers built-up in a flow cell were less uniform than those assembled in a beaker.

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1. Introduction

The layer-by-layer (LbL) technique is a simple and versatile method of assembling molecular films of nanometre dimensions [1–3]. Polyelectrolytes, colloids, proteins, deoxyribonucleic acid, viruses, ceramics and charged nanoparticles have all been successfully built-up on solid supports [1–5]. The technique provides precise control over the physical and chemical properties of the multilayer architectures by changes in the deposition conditions, for example by varying the ionic strength or pH of the solution [6]. LbL films can therefore be exploited for surface functionalization or for the fabrication of thin film devices [7].

Electrostatic interactions are the driving force behind the LbL process. The process of multilayer growth is controlled mainly by the charge density of the polyion pair used to assemble the organic film. Secondary non-electrostatic forces, such as hydrogen-bonding or hydrophobic interactions [8–12], may also influence the film formation. Atomic force microscopy, AFM, has been used increasingly to provide information on the outer surfaces of LbL films [13–18]. Moreover, investigations of the adsorption of single polyelectrolyte molecules is helping to elucidate the different phases of organization of the polyion layers and their changes in conformation (coil-to-globule) in a controlled environment [19–21].

We have previously described the use of polyelectrolyte LbL architectures for the chemical sensing of metals in solution [22–25]. The morphology of the organic thin films is thought to play an important role in determining their sensitivity and selectivity to different ions. Here, we report an AFM study of the outer surface of two of the structures used for sensing. Three different polyions, poly(ethyleneimine), PEI, poly(ethylene-*co*-maleic acid), PMAE, and poly(styrene sulfonic acid) sodium salt, PSS, were used to

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build the thin film architectures (three bilayer films in each case). These were prepared following either a traditional 'static' self-assembly in a beaker or a 'dynamic' self-assembly in a cell with a continuous flow of the different polyelectrolyte solutions.

2. Experimental details

Poly(ethyleneimine), PEI (M_w=25,000), and poly(styrenesulfonate), PSS (sodium salt, M_w=40,000), were obtained from Sigma-Aldrich. Poly(ethylene-*co*-maleic acid), PMAE (M_w=144,000), was purchased from Polysciences Inc. Aqueous solutions of concentrations 2×10^{-2} M for the PEI and 10^{-2} M for the PSS and PMAE were prepared in ultra-pure water. The measured pH was 8.1 for the PEI solution, 3.2 for the PMAE solution and 8.4 in the case of the PSS. In some experiments, tris(hydroxymethyl)aminomethane, $C_4H_{11}NO_3$ (tris), buffer solutions were also prepared. The pH of the buffer solution was set to 6.6 by the addition of HCl. A test of complex formation was first undertaken by mixing PEI, PMAE and PSS solutions under the conditions described above. While the separate cationic (PEI) and anionic (PMAE and PSS) solutions were clear, the mixtures were cloudy. This was seen as a good indication that the interaction between the polyion couple could result in the formation of a LbL multilayer. However, it should be noted that multilayer formation may be possible even if this mixing test is not apparently successful [7].

Approximately 50 nm of gold was deposited using physical vapour deposition, PVD, onto SF10 glass substrates (Hellma MA). Before the self-assembly procedure, the substrates were kept under vacuum. The polymer coating was prepared as reported in the literature [3,5] by alternately dipping the gold coated glass slides, first in PEI and then in PMAE, or PSS, for 15 min each. Two different deposition methods were used: (a) manual dipping in beakers containing the polymer solutions in ultra-pure water or buffer solution and (b) direct self-assembly in a flow cell, volume 2.65 ml, connected to a peristaltic pump, Fig. 1. In the latter case, the polyion solutions were allowed to flow uninterrupted through the cell. A flow of ultra-pure water or buffer solution was used after each adsorption to remove weakly attached material. The process of adsorption of the polyelectrolytes in the cell could be monitored using the technique of Surface Plasmon Resonance, SPR [3,5]. For the 'in-beaker' method, after each adsorption the thin films were rinsed in ultra-pure water or buffer solution. Films assembled in-beaker were dried in a nitrogen stream every two layers, while for the 'in-cell' assembly the films were dried only at the end of the process. Before being examined by the AFM, the organic films were kept in a sealed container under vacuum or in a clean room environment.

An Explorer™ atomic force microscope (Topometrix) was used to obtain images of the outer surface of the two different sensing films. The instrument was set to operate in the contact mode using a Contact AFM MLCT-EXMT-A, triangular shaped cantilever, with a silicon nitride tip coated in gold. The cantilever used had a length of 180 µm, a width of 18 µm, a thickness of 0.6 µm, a force constant of 0.05 N m^{-1} and a resonant frequency of 22 kHz. The gold coating provided high reflectivity. The tip was unsharpened with a typical radius of curvature <50 nm. All the scans were undertaken in air. Atomic force microscopy in contact mode is known to subject a surface to a mechanical stress, with the rastering tip constantly in contact with the sample. However, in the work described here, the use of a cantilever with a relatively low force constant allowed operation in this mode without apparent damage to the polymer surface.

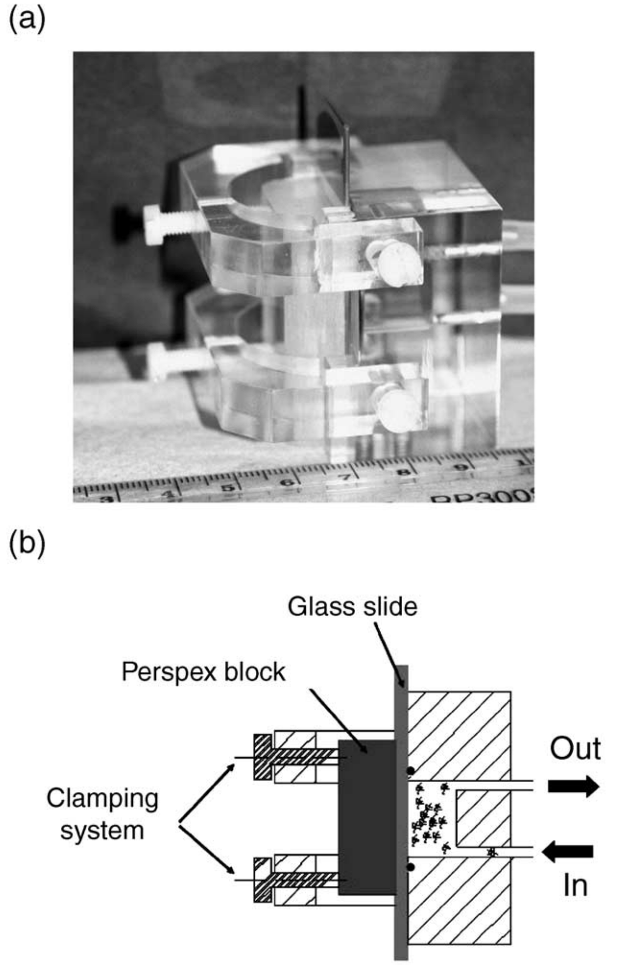

Fig. 1. (a) Photograph of the cell used for LbL deposition. (b) Cross section of the cell. A glass slide coated with a thin gold film is clamped and pressed against the cell (inner volume equal to 2.6 ml). Two Teflon tubes are connected to a peristaltic pump (not shown) and ensure a continuous flow of solution inside the cell.

3. Results and discussion

The first type of multilayer investigated was composed of three bilayers of PEI/PMAE. Poly(ethyleneimine), a weak polybase, is widely used as an adhesion promoter and was