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Report:

1. EXPERIMENTS ON SOLID LIQUID INTERFACE.

As such measurements were performed for the first time by our group, the validity of the approach was verified by performing reflectivity measurements using well-known samples, namely, 5 bilayers and 1 bilayer of barium behenate and 5 bilayer of octadecylamine (ODA) Langmuir-Blodgett films on silicon support. As the next step, measurements of thin films prepared by layer-by-layer (LBL) method were performed. X-ray reflectivity of these samples revealed a smooth, featureless curve excluding any reliable fitting and interpretation. We believe that the main reason of the lack of results is the very low contrast of the sample electron density with respect to the surrounding aqueous medium. In fact, the electron density of polyelectrolyte layers is very close to that of the aqueous solution. Therefore, we have tried a method to increase the electron density contrast between the deposited LbL layers and the surrounding water thus allowing the study of the LbL film structure while immersed in the liquid phase. The method is based on the inclusion ("decoration") of heavy metal ions into the layer.

Two types of samples were prepared. The first one contained the following sequence of layers:

 $(PEI - PSS)^{H_{2}O} - (PAH - PSS)^{H_{2}O} - (PAH - PSS)_{3}^{Cd^{2+}} - PAH^{Cd^{2+}}$

(the last layer being positive to enhance the successive electrostatic attachment of DNA). The first two polyelectrolyte bilayers were deposited from aqueous solutions of polyelectrolytes without any added salt, while successive three (PAH-PSS) bilayers were formed from solutions containing 0.25M CdCl2. The second type of samples was prepared from aqueous solutions of polymers. Two XRR measurements of the latter sample were done: the first one was performed immediately after its formation and the second one after treating of the multilayer in 0.25 M CdCl2 solution for 6 hours.



Fig. 1. Top panel: Experimental (points) and best fit (line) XRR data for LbL film scaled by the Fresnel reflectivity of Si/water interface as a function of Qz. Bottom panel: residues of the fit before DNA attachment (a), after attachment of double stranded DNA (b), after attachment of single stranded DNA (c).

Results of the experiments, performed before and after DNA layer attachment (doubleand single-stranded) are shown in Fig. 1. As it is clear, the suggested decoration method works well and DNA deposited by LBL method preserves its form (no denaturation takes place). Experiments on the hybridization have revealed impossibility of specific attachment of complimentary counterparts (manuscript was submitted to Langmuir). Other experiments on solid-liquid interface were performed on binding of different DNA samples to monolayer of ODA, namely, long DNA, short DNA, circular plasmid and open plasmid. It was found that the reflectrivity curves have significant differences for these samples. In particular, for circular plasmid the electron density of the DNA sublayer is lower and the roughness of the sample is much higher with respect to linear DNA, indicating the formation of less dense layer due to steric reasons.

2. AIR/WATER INTERFACE.

These experiments were performed for the investigation of the DNA length on the structure of the ODA-DNA complex formed at the air/water interface. Measurements were performed at different surface pressures (20, 30, 40 and 45 mN/m). for all cases it was found that the complex layer is more ordered for short DNA samples. The data are compared with independent measurements performed by ellipsometry (manuscript in preparation).