NANO HIGHLIGHT
Imaging Elemental Distribution Profiles with Long-period X-ray Standing Waves

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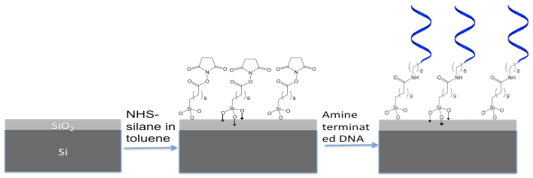
In biophysical solutions, the morphology and activity of negatively charged polymers DNA and RNA are intricately coupled to the surrounding cationic counterion layer that compensates and screens its charge. In addition to the biophysical relevance in bulk solutions, metal cation-polynucleotide (DNA/ssDNA or RNA) interactions at solid/liquid interfaces have recently attracted attention because of their importance in biosensor technologies. It is understood that metal ions interact with polynucleotides through long-range electrostatic forces and by binding to the nitrogenous bases and phosphate groups of the polymer backbone. However, experimental data on the extent and specificity of cation binding and/or the distribution of cations in the counterion layer is currently very limited for polynucleotides at the s/l interfaces and in bulk solutions. Therefore, in order to gain insights into cation-polynucleotide interactions, the Bedzyk, Geiger, Mirkin and Olvera Groups are collaborating to utilize X-ray methods, such as long-period X-ray standing waves (XSW) and anomalous small-angle X-ray scattering, to probe the counterion layer around substrate-tethered DNA at the solid/aqueous solution interface and DNA-coated gold nanoparticles in bulk solutions.

Building on findings from the Geiger Group, which developed the chemistry protocol for creating a DNA layer covalently linked to the native oxide layer of silicon substrates, the Bedzyk Group obtained quantitative structural characteristics and surface coverage for the 11-(trichlorosilyl)-undecanoic acid NHS-ester (NHS-silane) linker monolayer from recent X-ray reflectivity (XRR) measurements. For upcoming studies XSW studies on cation distribution around DNA at the solid/liquid interface, Bedzyk's group will functionalize the top SiO_2 surface of a Si/Mo multilayer X-ray mirror with DNA. The Si/Mo multi-bilayers have been sputter-deposited onto Si substrates by the optics group at the Advanced Photon Source. XRR characterization of these mutilayer substrates shows them to be suitable for XSW studies.

For the case of bulk solutions, preliminary X-ray scattering data from DNA-coated nanoparticles dispersed in RbCl aqueous solutions has been obtained at 3 different X-ray energies close to the K-absorption edge for Rb^+. The data is being currently analyzed to obtain the average radial distribution profile of the cation around the DNA-coated nanoparticle.



A self-assembled monolayer of NHS-silane is formed via covalent linkages between the silane terminus of the molecule and the oxide layer of Si. The formation of DNA layer from aqueous solutions proceeds via formation of amide bonds between the amine terminated DNA and the succinimide group of the linker layer. *Credit: Mark Bedzyk, Northwestern University*

[1] V. Kohli, M. J. Bedzyk, P. Fenter. "Direct Method for Imaging Elemental Distribution Profiles with Long-Period X-ray Standing Waves." *Phys. Rev. B* **81** (054112), 2010.