

Nanomechanical characterization of the surface stress of gold surfaces during the formation of DNA self-assembled monolayers

L.G. Carrascosa[†], M. Álvarez[‡], J. Tamayo^{*†}, C. Martínez-A[#] and L.M. Lechuga[†]

[†]Biosensors Group, Instituto de Microelectrónica de Madrid, IMM-CSIC, Isaac Newton 8 (PTM), 28760 Madrid, Spain,

[#] Department of Immunology and Oncology, Centro Nacional de Biotecnología (DIO-CNB-CSIC) Cantoblanco, 28049 Madrid, Spain

Sulfur group dependence on the formation of single stranded (ss) DNA self-assembled monolayers (SAMs) on gold surfaces has been studied by the cantilever bending method. The studied oligonucleotides were modified with a thiol molecule (SH-DNA), a symmetrical disulfide carrying two identical ssDNA molecules (DNA-SS-DNA) and an asymmetric disulfide carrying the protecting group dimethyltrityl (DNA-SS-DMTO). The surface stress induced by the adsorption of the modified oligonucleotides on gold critically depended on the organosulfur linker used. Thus, the mean values of the surface stress were 20, 15 and 9 mN/m for SH-DNA, DNA-SS-DMTO and DNA-SS-DNA, respectively. In addition, kinetics measurements show that both types of ssDNA disulfides adsorb 30% more slowly than the thiol-modified ssDNA. Subsequent adsorption of mercaptohexanol (MCH) on the preformed ssDNA monolayer also showed a different adsorption profile. MCH induced surface stress was of about 10, 20 and 31 mN/m for preformed SAMs of SH-DNA, DNA-SS-DMTO and DNA-SS-DNA, respectively. The critical role of the organosulfur linker on the ssDNA monolayer is supported by fluorescent experiments. We interpret the results using a two-step adsorption model, in which the oligonucleotides quickly physisorb on the gold before the chemisorption is achieved via formation of the same alkanethiolate species. This implies the disulfide cleavage for the disulfides. The cantilever bending upon adsorption is related to the transition between the physisorbed and chemisorbed states, in which the disulfide modification imposes a major difficulty to achieve the chemisorbed state due to geometrical and steric constraints. We conclude that the surface stress induced by ssDNA adsorption is approximately proportional to the surface density of chemisorbed ssDNA.

*Corresponding Author. E-mail address: jtamayo@imm.cnm.csic.es. Phone: +34 918063338