

## Investigation of Bio-Molecular Interfaces Using Photoemission Spectroscopy In Combination With In-Situ Deposition Techniques

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**INTRODUCTION:** The presented research is motivated by the increasing incorporation of bio-materials in electronic and sensor devices. As bio-materials are used in concert with other materials to form device structures, their interfaces to these materials become a matter of interest. Chemical and electronic properties of contacts crucially define the properties of such structures. Photoemission spectroscopy (PES) has traditionally been a method of choice to explore interfaces of a great variety of materials. However, since in such experiments, the interface of interest needs to be prepared in vacuum to avoid interference with ambient contaminants, bio-materials interfaces have been difficult to investigate in the past. Since bio-molecules usually cannot be evaporated in vacuum due to their thermal fragility, interfaces can in many cases only be fabricated from solution (spin coating, dipping, etc...), which cannot be done in vacuum. The presented experiments address this challenge through the integration of an electro-spray based thin film deposition system [1] into a commercially available photoemission spectroscopy system outfitted with a directly attached glove box. Using this set-up, the electronic structure of ribonucleic acid (RNA) homopolymer [2] and L-cysteine [3] interfaces with graphite and gold were investigated.

**METHODS:** Details about the experimental methods can be found in Ref.[1]. Briefly, RNA and L-cysteine were deposited in several steps using electro-spray or dipping in inert atmosphere. In between deposition steps PE-spectra were measured resulting in series of spectra detailing the development of the electronic and chemical structure at the interface. Evaluation of these sequences allowed drawing the orbital line-up at the contacts, and gave insight into the chemical interaction at the interface.

**RESULTS:** As an example, Fig.1 shows ultraviolet photoemission spectroscopy (UPS) spectra of the highest molecular orbitals (HOMO) of polyguanosine (poly rG) and polyuridine (poly rU) representative for purine and pyrimidine spectra. Poly rG shows a shoulder at the low binding energy side of the spectrum, which is not

present in the poly rU spectrum. This indicates a smaller ionization energy of poly rG compared to poly rU.

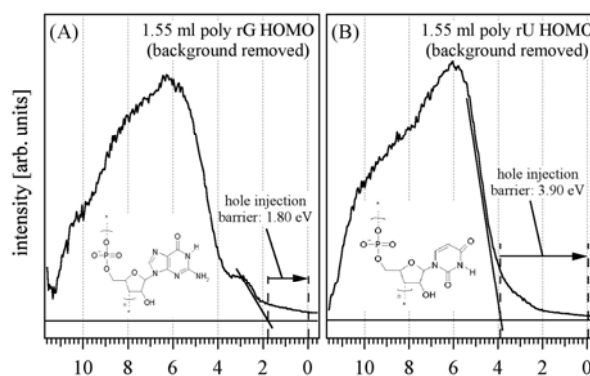


Fig.1: HOMO spectra of polyguanosine (poly rG) and polyuridine (poly rU). A smaller hole injection barrier is evident for poly rG.

**DISCUSSION & CONCLUSIONS:** Our results demonstrate the application of electro-spray as an in-situ deposition technique for the preparation of largely contamination free bio-molecular thin films for surface scientific investigations. Electro-spray enables clean repeat deposition of thin films directly from solution without breaking the vacuum. Our results on RNA homopolymers indicate significant differences in ionization energies, where poly rG has the smallest and poly rU the largest. This directly influences the injection barriers relative to HOPG and Au, indicating that charge transfer crucially depends on the particular nucleotide in contact with an electrode. Our experiments on the L-cysteine/Au interface indicate the formation of an interface state caused by the chemical interaction between thiol group and Au surface. This state could potentially act as a “stepping stone” for charge transfer between proteins and Au.

**REFERENCES:** [1] N. Dam, M.M. Beerbom, J.C. Braunagel and R. Schlaf: *J. Appl. Phys.* 97 pp.024909 (2005). [2] N. Dam, B.V. Doran, J.C. Braunagel and R. Schlaf: *J. Phys. Chem.* 109 (2), pp.748-756 (2005). [3] M.M. Beerbom, R. Gargagliano and R. Schlaf: *Langmuir* 21 (8), pp.3551-3558 (2005).

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