Title: “Adsorption and Co-Adsorption of DNA Bases on Gold Electrodes”

Electrode-electrolyte interfaces allow mimicking the electrostatic properties of biological interfaces. Therefore, they constitute a suitable platform to study the influence of static electric field on the properties of biologically relevant molecules. The right genetic replication involves the interactions between complementary DNA bases that are more favorable than the interactions between non-complementary bases. There are theoretical, spectroscopic and crystallographic studies that suggest that cytosine-adenine discordant DNA sequencing is due to the presence of "unstable" tautomeric forms ("rare tautomers"), able to overcome the mechanisms for detecting inconsistencies1–3.

The combination of classical electrochemical techniques with ‘in situ’ spectroscopy and scanning probe microscopy can help to obtain both phenomenological and structural information of the behavior of DNA bases on gold electrodes, including the tautomeric and acid-base equilibria, and the interactions between co-adsorbed bases.

The study by ATR-SEIRAS and quantitative SNFITIRS of the chemical adsorption of adenine on gold electrodes has shown that the molecule interacts with the electrode by the amine nitrogen N10 and the pirimidinic ring nitrogen N1. It adopts a tilted orientation relative to the surface and rotates with the potential to favor the interaction between its permanent dipole and the static electric field. On the other hand, the chemical adsorption significantly modifies the first pKa of adenine while remains nearly unaltered the value of the second pKa.

Thymine adsors in anionic form on gold electrodes, with the molecular plane oriented normal to the electrode surface. The comparison of the in situ ATR-SEIRA with the theoretical spectra obtained from DFT calculations showed that the tautomeric nature of the adsorbed species is pH dependent.

Adsorbed cytosine adopts also a perpendicular orientation relative to the electrode. The chemical adsorption process modifies the tautomeric equilibrium of cytosine in solution, favoring the keto-imino tautomer in adsorbed state in comparison with the keto-amino form that is predominant both in solution and in physically adsorbed state.

Regarding the co-adsorption of complementary basis adenine-thymine, the spectroelectrochemical results indicate that the interaction with the complementary base induces changes in the orientations with respect to the electrode of the previously adsorbed one. It seems that the pyrimidine base of the pair adopts a parallel orientation of the molecular plane relative to the electrode, while the purine base maintains its inclination or even increases it. In addition, the presence of thymine causes an increase in the surface excess of adenine previously adsorbed on gold.

References

Coffee & Timbits will be served at 1:30 p.m.
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