

SELF-ASSEMBLED MONOLAYERS OF PEPTIDE NUCLEIC ACIDS (PNA) ON DIFFERENT SURFACES.

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The understanding of the structure of molecular layers is of a great importance because its atomic arrangement determines the mechanical properties, electronic behavior and reactivity of the surfaces. Therefore, the ability to control the surface structure at an atomic level is a crucial point, not only for designing new materials for catalytic applications, electrodeposition or corrosion prevention, but also in the development of the wide field of nanoscience and nanotechnology.

Self-assembled monolayers (SAMs) of alkanethiols have been widely studied due to their relevant technological properties. Based on such knowledge, thiolated DNA has been immobilized on surfaces, although it usually forms disordered formless globular structures with reduced bioactivity, or requires the co-immobilization of spacer thiols leading to mixed monolayers. Here we report on the formation and structural characterization of ordered SAMs of the DNA analogous peptide nucleic acid (PNA). PNA is an achiral and uncharged DNA mimic of high biological and chemical stability. We illustrate that, in spite of their remarkably long length of up to 7 nm, cysteine-modified ssPNA oligomers assemble by themselves standing-up on gold surfaces similarly to the SAMs of short alkanethiols [1].

Furthermore, we have been able to immobilize and to study ssPNA molecules on more realistic surfaces, as different kinds of mineral pyrite. These studies have great implication for the understanding of the catalytic role of surfaces in the origin of life.

Therefore, in this work we present a thorough spectroscopic and morphological characterization of self assembled monolayers (SAMs) of thiol-derivatized Peptide Nucleic Acid (PNA) chains adsorbed on gold and pyrite surfaces by using Reflection Absorption Infrared Spectroscopy (RAIRS) and X-ray Photoelectron Spectroscopy (XPS) techniques. We have found that molecular orientation of PNAs strongly depends on surface coverage. In the case of gold, at low coverage PNA chains lie flat on the surface, while at high coverage PNA molecules realign their molecular axes with the surface normal and form SAMs without the need of co-immobilization of spacers or other adjuvant molecules. The change in the molecular orientation has been studied by infrared spectroscopy and it has been confirmed by Atomic Force Microscopy (AFM). PNA immobilization has been followed by analyzing the N(1s) XPS core level peak. We show that the fine line shape of the N(1s) core-level peak is due to a chemical shift rather than to the presence of different adsorption sites. A combination of the above mentioned techniques allow us to affirm that the structure of the SAMs is stabilized by molecule-molecule interactions through non-complementary adjacent nucleic bases. Furthermore, BioSAMs of ssPNAs maintain their capability for recognising

complementary ssDNA, and their specificity is such that they act as biosensors able to discriminate even a point mutation in target ssDNA. We have also successfully adsorbed PNA on a mineral pyrite surface, which plays an important role on the origin of life. Therefore, we will show a comparison study between molecular behavior on both surfaces: gold and pyrite.

These structural and functional results have been obtained from a complementary powerful label-free techniques for surface characterisation such as synchrotron radiation based X-ray photoemission spectroscopy (XPS), X-ray absorption near-edge spectroscopy (XANES), atomic force microscopy (AFM) and reflection absorption infrared spectroscopy (RAIRS).

References:

[1] C. Briones, E. Mateo-Marti, C. Gomez-Rodriguez, V. Parro, E. Roman, J.A. Martín-Gago, *Physical Reviews Letters*, **93** n°20 (2004) 208103.