NANOSTRUCTURED MOLECULAR SURFACES AND ULTRATHIN FILMS

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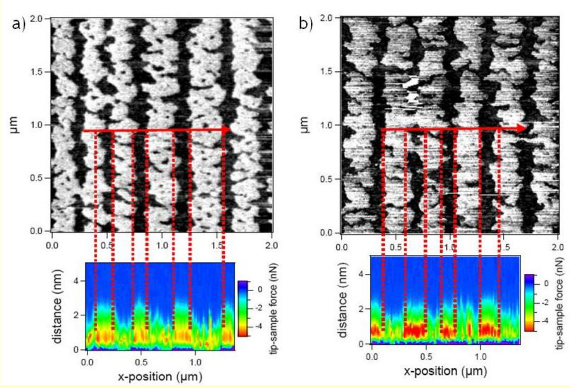

Dynamic force spectroscopy images of stripes and channels in LB films of DPPC (see research line 1).

Surface and thin film nano-structuring has an increasing importance in modern science and technology, being the key to develop future nano-electronic devices, functional nano-biodevices, molecular machines, etc. Fabrication and investigation of nanostructuring strategies involve synergism of chemistry, physics, materials science, and biology.

Keywords: Nanotechnology, Molecular Surfaces, Ultrathin films, Surface Spectroscopies.

RESEARCH LINES

1 – Nanostructuring strategies for biofunctional surfaces (*G.M.L. Messina, G. Marletta)*

This line is aimed to establish new strategies to achieve the nanostructuring of ultra-thin polymer films. In particular, a first strategy has been set-up to fabricate well-ordered nanostructured phospholipid/polymer films over large areas by the using Langmuir-Blodgett (LB) technique to obtain uniform and defect-free films, to be used as platforms to engineering biological interfaces. Langmuir-Blodgett technique is used to obtain a regular patterned large-area with mesostructured features, consisting in periodic, self-organized L-α-dipalmitoylphosphatidylcholine (DPPC) monolayer patterns with feature sizes down to 100 nm over areas of square centimeters area. Phase transitions from a liquid-condensed (LC) to a liquid-expanded (LE) phase in the LB film are used to create a pattern consisting of alternating LC stripes, 800 nm wide, separated by 200 nm wide channels (see fig. 1 above). Size and shape of the DPPC patterns can be controlled by adjusting the deposition parameters. Selective segregation of a different component within the channels has been demonstrated. Further applications as biofunctional surfaces are currently explored.

A second strategy has focused the production of nanopore arrays in polymer matrix, in view of applications as chemical nanocontainers, confining structures for nanophotonic and nanoelectronics, etc…The strategy is based on an entrapment-and-removal process of templating inorganic nanoparticles within polymeric films. The selective removal of the inorganic nanoparticles leads to the desired 2D-nanopore arrays, combining chemically different bottom and walls. The nanopores depth was modulated by using irradiation methods. Selective adsorption of proteins, e.g., Human Lactoferrin (Lf) and Human Serum Albumin (HSA), has been demonstrated within the nanopore or the walls. Applications in nanobiosensing and protein mixture separation are currently explored.

2 – Substrate Induced Ordering in Poly(3-hexylthiophene) Thin Crystalline Films (G. Li Destri, G. Marletta)

This line of research is aimed to control the crystalline ordering in polymeric ultrathin films by changing the substrate chemical structure. The effect of different substrates on the crystalline structure of thermally annealed poly(3-hexylthiophene) (P3HT) thin films was investigated by atomic force microscopy (AFM) and grazing incidence X-ray diffraction analysis (GIXRD). The average orientation of the lamellae, after annealing, markedly differed as a function of the interfacial energy with better reciprocal and in plane orientation of the lamellae onto hydrophobic substrate than on hydrophilic ones. Fast Fourier Transform of AFM images showed a preferential alignment direction of close packed lamellae on hydrophobic substrates. The effect is interpreted in terms of the different interface free energy between the polymer and the substrates, affecting the molecular mobility and, in turn, the P3HT crystallization features. The effect on the charge transport mechanism and, in turn, on the efficiency of P3HT-based field effect transistors is currently investigated.

3 – Hybrid bilayer of sputtered gold nanoparticles onto diblock-copolymer template (V. Torrisi, G. Marletta).

This line is aimed to construct nanometric thick hybrid bilayers based onto block copolymers and sputtered gold layers. Self-assembled di-block copolymer films were prepared by using the Horizontal Precipitation Langmuir-Blodgett (HP-LB) method, obtaining highly homogeneous nanostructured monolayers of PAA-*b*-PnBuA di-block copolymer. The phase-separation of the PAA-*b*-PnBuA film before and after gold sputtering and the effect of the chain mobility onto the organization of gold atoms were studied by heating at $T>T_g$. The nanoparticle distribution onto the block copolymer domains, studied by Atomic Force Microscopy and Time of Flight Secondary Ion Mass Spectrometry, seems strongly affected by the annealing. In particular, annealed hybrid bilayers exhibit memory effects, also if annealing at T >Tg doesn't induce polymer mixing between two blocks or between blocks and gold. The films show rather surprising Schottky-like I-V characteristics, peculiar of the formation of hybrid polymer-metal junctions.

International Collaborations

Institute of Materials Science and Technology, Friedrich-Schiller-Universität, Jena – Germany; Biological Physics Laboratory, University of Manchester, Manchester, U.K.; Departamento de Física Aplicada and Departamento de Biología Molecular, Universidad Autónoma de Madrid, Cantoblanco-Madrid, Spain; Department of Physics and Astronomy, University College London and London Centre for Nanotechnology, London, UK; Institut de Science et d'Ingénierie Supramoléculaires (ISIS), Université Louis Pasteur, Strasbourg (France); Department of Biomaterials, University of Brema (De).

Selected Publications

- **"Evaluation of Plasma Modified Polycaprolactone Honeycomb Scaffolds by Human Mesenchymal Stem Cells Cultured in Vitamin D Differentiation Medium"** by F.Formosa, V. Sanchez Vaquero, C. Rodríguez Navas, Á. Muñoz Noval, N. Tejera Sánchez, M. Manso Silván, J. P. García-Ruiz, G. Marletta; Plasma Proc. Polym., 7 (2010) 794-801.
- **"Molecular Modelling of Oligopeptide Adsorption onto Functionalised Quartz Surfaces"** by G.Forte, A.Grassi and **G.Marletta**; J. Phys. Chem. B 111 (2007) 11237- 11243.
- **"Patterning of Lactoferrin Using Functional SAMs of Iron Complexes"** by N.Tuccitto, N.Giamblanco, A.Licciardello and G.Marletta; Chem.Comm. 25 (2007) 2621-2623.
- **"Expression of cell adhesion receptors in human osteoblasts cultured on biofunctionalized poly-(ε-caprolactone) surfaces"** by I.Amato, G.Ciapetti, S.Pagani, **G.Marletta**, N.Baldini, D.Granchi; Biomaterials 28 (2007) 3668 - 3678.
- **"Phase Segregation in Thin Films of Conjugated Polyrotaxane- Poly(ethylene oxide) Blends: A Scanning Force Microscopy Study"** by L. Sardone, C. C. Williams, H. L. Anderson, G. Marletta, F. Cacialli , P. Samorì; Adv. Funct. Mater., 17 (2007) 927-932.
- **"Human bone marrow stromal cells: In vitro expansion and differentiation for bone engineering"** by G. Ciapetti, L. Ambrosio, **G. Marletta**, N. Baldini, A. Giunti; Biomaterials 27 (2006) 6150-6160.