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Electrochemical and X-ray photoelectron Spectroscopy measurements for SAMs characterization

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Self-assembled monolayers (SAMs) were widely studied in the last decades, gaining an increasing interest thanks to their implementation in different bioelectronic devices as surface plasmon resonance (SPR) and field-effect transistors (FETs) [1,2]. SAMs growth for biosensor application consists in a mixed SAM, where a longer chain is used to anchor the biorecognition element and a shorter one as spacer, increasing both the functionalization yield and the performance of the final devices. Mixed SAMs were exploited in the gate electrode development for biosensors based on electrolyte gated organic field-effect transistors (EGOFETs), able to reach the physical limit of sensitivity [3]. In similar devices SAMs are typically used to efficiently immobilize the biorecognition element [4], but Macchia et al. also hypothesized a role in improving device performance thanks to the formation of a diffuse hydrogen bonding network between chains [3].

In this regard, a combined strategy of electrochemical and X-ray photoelectron spectroscopy (XPS) experiments was carried out. This approach was used to investigate of SAMs conformational reorganization onto an electrode surface due to the application of an electrical field [5]. In particular, 3-mercaptopriopionic acid SAM (3MPA SAM) modified gold electrodes were activated with a 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and N-hydroxysulfosuccinimide (NHSS) (EDC/NHSS) by shortening the activation time, from 2 h to 15/20 min, labelled as Protocol-A, -B and -C, respectively. In fact, this step plays a key role in the reaction yields (formation of N-(2-hydroxyethyl)-3-mercaptopropanamide, NMPA) but also in the conformational rearrangement observed during the application of the electrical field [6,7]. Moreover, differential pulse voltammetry (DPV) in NaOH 0.1 M is used to estimate the reductive desorption of functionalized SAMs.

These results were compared with well-known trend available for other SAM structures for correlating supramolecular behaviour of the SAM due to the electric field application with performance of EGOFETs biosensors.

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