

Focused Ion Beam Treatment of Self-Assembled Monolayers for Protein Patterning

N. Giambianco, N. Tuccitto, A. Licciardello, G. Marletta¹.

¹ *Dip. di Scienze Chimiche- Università degli studi di Catania, A .Doria, 6, 95125, Catania Italy.*

INTRODUCTION: Patterning of protein on surfaces is a topic of great interest for many applications including biosensors and bioelectronic devices¹. The formation of protein patterns requires surfaces combining the resistance to unspecific surface adsorption with spatially-resolved specific binding interactions. In this paper we report a new protein patterning method involving the use of Focused Ion Beams (FIB) combined with metal complex-based self-assembled monolayers (SAM).

METHODS SAM of 11-mercapto-1-undecanol (MUO) was prepared on polycrystalline gold. The MUO-SAM was etched with the focused gallium ion beam to produce square regions of bare gold. Such regions were covered with a mixed² component SAM containing terpyridine ligand that upon reaction with an iron (II) salt produces the iron-terpyridine complexes. The patterned substrate was then incubated with Lactoferrin (LF) 10 µg/ml in millipore H₂O. The adsorption behaviour of LF from aqueous solution on the surface-anchored iron complex and for comparison, onto the original SAM as well as onto the MUO-SAM has been studied *in situ* by means of Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)⁴. The spatial selectivity of LF adsorption has been demonstrated by using ToF-SIMS chemical imaging.

RESULTS: The QCM-D adsorption curves of LF on the iron-containing SAM were indicative of remarkable and very fast adsorption. On the contrary, a lower but detectable adsorption also occurred in the case of LF on MUO and terpyridine based SAM. The ToF-SIMS chemical maps of the patterned surface before (Fig.1a,b) and after (Fig.1c) LF adsorption results are shown in Fig. 1. In particular, Fig. 1b demonstrates that iron has been selectively fixed on the terpyridine-containing areas (the squares in Fig. 1a) whereas the remaining surface, still covered by the MUO-SAM, is iron-free. Fig. 1b shows that stable protein adsorption occurred selectively on the iron-containing patterns.

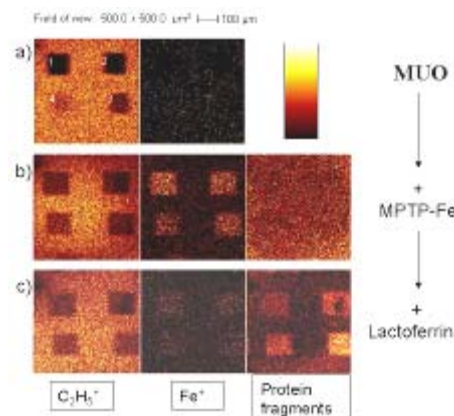


Fig. 1: ToF-SIMS imaging of patterned surface. a) MUO self-assembled monolayer, b) iron complex SAM, c) lactoferrin-treated surface. Numbers in the top-left image indicate ion dose :1>2>3>4.

DISCUSSION & CONCLUSIONS: QCM-D and ToF-SIMS measurements showed that LF monolayers can be selectively and stably adsorbed on the iron-containing areas, but not on the OH-terminated alkanethiol SAM. In conclusion, we developed a bottom-up method for preparing surface patterns of LF by specific non-covalent interactions between the native protein and an iron-terpyridine complex-based SAM.

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