Biosensors and Bioelectronics 53 (2014) 154–159

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Atmospheric pressure plasma polymers for tuned QCM detection of protein adhesion

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ARTICLE INFO

Article history:
Received 17 July 2013
Received in revised form
28 August 2013
Accepted 17 September 2013
Available online 27 September 2013

Keywords:
Plasma polymerization at atmospheric pressure
Thin films
Protein absorption
Quartz crystal microbalance—QCM

ABSTRACT

Our efforts have been concentrated in preparing plasma polymeric thin layers at atmospheric pressure grown on Quartz Crystal Microbalance—QCM electrodes for which the non-specific absorption of proteins can be efficiently modulated, tuned and used for QCM biosensing and quantification. Plasma polymerization reaction at atmospheric pressure has been used as a simple and viable method for the preparation of QCM bioactive surfaces, featuring variable protein binding properties. Polyethyleneglycol (ppEG), polystyrene (ppST) and poly(ethyleneglycol–styrene) (ppST–EG) thin-layers have been grown on QCM electrodes. These layers were characterized by Atomic Force Microscopy (AFM), Contact angle measurements, Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). The plasma ppST QCM electrodes present a higher adsorption of Concanavalin A (ConA) and Bovine Serum Albumin (BSA) proteins when compared with the commercial coated polystyrene (ppST) ones. The minimum adsorption was found for ppEG, surface, known by their protein anti-fouling properties. The amount of adsorbed proteins can be tuned by the introduction of PEG precursors in the plasma discharge during the preparation of ppST polymers.

1. Introduction

Protein adsorption on the polymeric surfaces plays a key role in chemistry and biology and has therefore promoted a widespread interest in many biomedical applications like implants, biosensors, etc. (Karlsson et al., 2005; Rabe et al., 2011; Vogler, 2012; Goddard and Hotchkiss, 2007). The immobilization of proteins on the surfaces as part of the biosensor fabrication process implies a favorable orientation and stability of the surface-immobilized biomolecules with the high-functionality (Karlsson et al., 2005). The main challenge is the retention of biological native activity. Direct immobilization can be accomplished by different routes including electrostatic interaction (Rabe et al., 2011) hydrophobic interaction (Vogler, 2012), covalent bonding and specific interaction (Goddard and Hotchkiss, 2007). Within this context, surface based systems for biosensing in terms of real-time label-free measurement of biological interactions have been developed. They exploit the electro-optical properties of metals (Surface Plasmon Resonance—SPR), piezoelectric properties (Quartz Crystal Microbalance—QCM) and electrochemical transduction (Mahon et al., 2012; Voinova et al., 2002). In QCM biodetection, biofunctional thin films may be adsorbed on the QCM crystal surface with the added possibility of tuning polymer composition in order to control the binding. Various polymeric layers and coating procedures have been used to enhance QCM sensitivity and strong non-specific binding is mostly occurring on hydrophobic polymers.

It is known that polyethyleneglycol (PEG) coatings are used for protein-repelling, hindering their attachment on surfaces (Niidome et al., 2006; Tessmar and Gopferich, 2007; Hoffman, 2002; Liqiong et al., 2006). However, the major disadvantage with PEG thin polymeric films is related to their low stabilities when exposed to aqueous solutions. One way to circumvent this problem is to combine PEG and hydrophobic polymers, i.e. polystyrene or to increase the cross-linking ratio of the resulted hybrid polymers.

Atmospheric pressure plasma polymerization represents a useful technological solution to these issues and has unique practical advantages: (i) ultrathin film deposition, (ii) good adhesion to the substrate and (iii) formation of highly stable surfaces Silvan et al., 2004.

With all these in mind, herein our efforts have been concentrated in preparing under plasma at atmospheric pressure, QCM electrodes casted with polyethylene glycol-like (ppEG) and polystyrene (ppST) or composite poly(ethylene glycol–styrene) (ppST–EG) thin layers grown by using pure or a mixture of styrene and ethyleneglycol

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http://dx.doi.org/10.1016/j.bios.2013.09.035