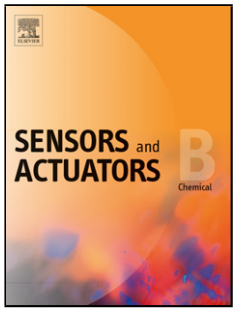

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Integration of Core/Shell Nanoparticle and QCM-D Sensors in a Single Device: A New Approach to the *In Situ* Detection of Solvent Content in Thin Adsorbed Films with Minimized Response to Spurious Bulk Refractive Index Changes

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Abstract

A combined optical and acoustic wave based setup for the time-resolved determination of solvent content in thin adsorbed layers is presented. Implementation of the novel device is achieved by forming a core/shell nanoparticle sensor based on localized plasmon resonance directly on the surface of a quartz crystal microbalance (QCM) integrated in commercially available QCM-D instrumentation. A peculiarity of the optical sensor is the presence of a "magic angle", under which changes of the bulk refractive index of the adjacent media do not influence the sensor response. Kinetic studies of fibrinogen adsorption with the combined setup and the optical sensor set to the magic angle show that the surface-bound films contain a considerable amount of water with a dry/wet mass ratio of about 26%. Comparison to literature values suggests that the water molecules are not only firmly bound to the proteins in form of a hydration shell but also entrapped in interstitial regions of the adsorbate. The high water content detected in the films confirms the importance of the presented approach. Direct comparison of the adsorption kinetics for dry and wet mass reveals that water entrapment occurs on a longer time scale than mere protein binding.

Keywords: Surface plasmon resonance, QCM-D, core/shell nanoparticles, self-assembly, solvent content, protein layer.

1. Introduction

Soft functional films at the solid-liquid interface play a significant role in biotechnological and biomedical applications. For example, substrate-bound lipid layers with incorporated membrane proteins as well as hydrogels of well-defined stiffness have been used to control