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FUNCTIONALIZED POLYMER MEMBRANES FOR PLASMONIC SENSING WITH ENHANCED SELECTIVITY

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Abstract

We investigate theoretically and experimentally the concept of enhancing the selectivity of chemical, biochemical and biological (nano)plasmonic sensors utilizing multifunctionalized polymer membranes. Membrane nanocompositing is done by lamination and surface/pore immobilization. A separator/filter and an affinity-based adsorption enhancer are integrated into a single multifunctional membrane structure. Functionalized membrane may be transferred across platforms and even used for different types of sensing devices.

Introduction

Surface plasmon optics is the basis for a novel generation of ultra-sensitive (bio)chemical and biological sensors that are label-free and ultrafast [1]. Typically their active part is a surface composed of metal or metal-dielectric (plasmonic metamaterial) [2] with a negative real part of the relative dielectric permittivity. Two distinct types of surface plasmon resonance are used for such sensing, one of them based on propagating surface waves (surface plasmon polaritons, SPP), the other on nonpropagating (localized) SPP [3]. In both cases analyte particles adsorb on the active surface, modifying the conditions for the existence of SPP. In its basic configuration a plasmonic sensor is thus a refractive index sensor. Its sensitivity may well exceed 10^{-8} refractive index units, i.e. 1 ng/cm^2 (0.003 monolayer) [4].

A problem with plasmonic sensors in their basic form is their relatively low selectivity based solely on refractive index changes, so that different materials with similar refractive indexes cause similar outputs. An approach to overcome this problem is functionalization of the sensor surface by nanocompositing [5]. Here an interaction partner ("ligand") is immobilized to the sensor surface, serving as affinity-based binding material for the target analyte. Another way is to utilize a filter or separator to remove undesired species and allow only the target analyte to reach the sensor surface [5]. Membranes are often used for this, while the separation mechanism may be based on nanopores (e.g. molecular sieves) or nonporous (dense) structures with solution-diffusion mechanism. Built-in electrical charges within the membrane may be also utilized (e.g. ion exchangers).

In this work we investigate the possibility to integrate the separator/filter structure and the affinity-based target-specific adsorption enhancer into a single membrane structure which may further be merged with the sensitive plasmonic

adsorption [6] and enzyme immobilization [7]. Fig. 2a shows a scanning electron micrograph (SEM) of the poly(GMA-*co*-EGDMA) surface.

For the formation of membranes comprising GMA as a precursor for subsequent functionalization we selected a new method recently described in literature [8-9]. It combines a traditional immersion precipitation process for making membranes with photopolymerization and crosslinking of functional monomers included in the casting solution. As the environmental SEM micrograph of the top surface in Fig. 2b shows, the resulting membranes have an integral top skin layer with fine selective channels over a coarser mechanically stable support. The top skin layer has a separation function against undesirable species present in the feed solution. Subsequent functionalization of the epoxy groups entrapped within the membrane provides ligand sites for enhanced plasmonic sensing.

Conclusion

Possibilities to integrate separator and ligand for plasmonic sensor into a single structure are considered. The multifunctionalization ensures a highly tailorable element that is transferable across platforms. This allows for a multiple use of a single sensor type for a larger number of different analytes or massive process parallelization using the identical plasmonic structure as the basic element. At the same one may use built-in (nano)pores to augment the effective surface for adsorption and thus vastly increase the amount of adsorbate, furnishing a further increased sensitivity. Additional reaction enhancements may also be incorporated, including but not limited to catalyst particles. The approach may be extended to other types of chemical and bio sensors.

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