PHYSICAL CHEMISTRY 2012

11th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Under the auspices of the
University of Belgrade

Proceedings

The Conference is dedicated to
Professor Ivan Draganić

September 24-28, 2012
Belgrade, Serbia

ISBN 978-86-82475-27-9 ***Volume*** **1**
ISBN 978-86-82475-28-6 ***Volume*** **II**

Title: PHYSICAL CHEMISTRY 2012 (Proceedings)
Editors: S. Anić and Ž. Čupić
Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: "Jovan" Priting and Publishing Company; 200 Copies;
Number of pages: 6+ 497; **Format**: B5; Printing finished in September 2012.

Text and Layout: "Jovan"

200- *Coppy printing*

H-25-P

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

structure itself. We consider both interface and pore modification of membranes towards enhanced device selectivity.

Multifunctionalization

A structure of a plasmonic sensor is schematically shown in Fig. 1a. A surface with negative effective value of relative dielectric permittivity is the sensing part. An enhanced selectivity structure may contain separator and immobilizing structure, the latter fully immersed in the SPP field. Fig. 1b shows two approaches to integration of the separator (a porous membrane) and affinity blocks: surface-based (left) and bulk-based (right).

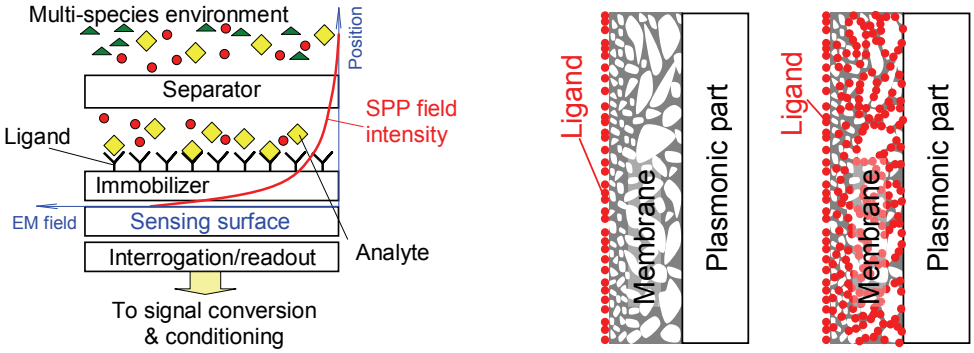

Figure 1. a) Schematic presentation of plasmonic chemical sensor; b) two approaches to integration of separator and ligand (surface and bulk immobilization)

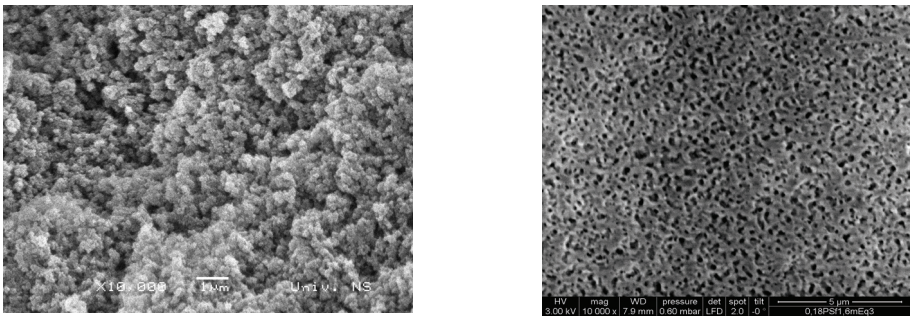

Figure 2. a) SEM picture of porous poly(GMA-*co*-EGDMA) surface. b) ESEM image of the top surface of an asymmetric membrane made by photopolymerization.

Experimental

We chose macroporous crosslinked copolymers (MCP) which are readily formed into membranes and keep a permanent well-developed porous structure. Particularly we used glycidyl methacrylate (GMA)-based MCP. The attractiveness of GMA for affinity-enhanced sensing originates from the presence of an epoxy group in GMA molecule that can easily be transformed into various functional groups, like amine, iminodiacetate, thiol, dithiocarbamate, pyridine, etc., making it a multipurpose material. GMA was already successfully used for heavy and precious metals

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 fuctionalization 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.

Acknowledgment

This work has been funded by Serbian Ministry of Education and Science within the framework of the projects TR32008 and III 43009.

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