Summary of Ph.D. dissertation

Title: "Macroporous films of conducting molecularly imprinted polymers (MIPs) as recognition units of chemosensors for selective detection and determination of chosen biorelevant compounds".

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The present Ph.D. dissertation describes a fundamental research aiming at development of procedures of fabrication of macroporous films of molecularly imprinted polymers (MIPs) and their application as recognition units of improved chemosensors for determination of chosen biologically relevant compounds.

Each chemosensor comprises two major units, namely, a recognition unit and a transduction unit. The latter transduces a chemical recognition event into an analytically useful signal. MIP films prepared within the present research were applied as highly selective recognition units. One of main problems of the MIP technology is slow permeation of an analyte through an MIP film. Herein, fabrication of macroporous films of a regular and open structure resulted in substantial improvement of analytical performance of the chemosensors fabricated. Namely, their sensitivity and the limit of detection (LOD) were improved. In the present research, an electrochemical quartz crystal microbalance, EQCM, (piezomicrogravimetric chemosensors) and extended-gate field-effect transistors, EG-FETs, (electric chemosensors) were applied as signal transducers.

Herein, chemosensors for enetioselective determination of D- and L-arabitol were devised and fabricated. In the future, they may be applied for early diagnosis of infections caused by yeasts *Candida* sp. Reversible formation of ester bonds between boronate groups of functional monomers and hydroxyl groups of templates was exploited in the strategy of molecular imprinting of these sugar analytes in MIP films. Moreover, other chemosensors, selective to a protein, namely, human serum albumin (HSA) were devised. To reach this goal, an improved synergistic strategy combining (i) semi-covalent imprinting of proteins, (ii) surface imprinting and (iii) fabricating of inverse opals was applied. In effect, all imprinted molecular cavities were localized exclusively on inner walls of macropores. Furthermore, all recognizing sites of functional monomers were exclusively located inside molecular cavities at positions complementary to those of binding functional groups of HSA.

The present research comprised two stages, namely, (i) designing and preparing chemosensors including characterization of the MIP films and (ii) determination of analytical parameters of the chemosensors including evaluation of the chemosensors for practical applications. MIP films were deposited on the transducer surfaces by electrochemical polymerization. Macroporosity of the films was generated by templating the transducer surfaces with colloidal crystals of silica nanobeads with 330 or 500 nm diameter. The procedure developed consisted of the following steps. (i) On the transducer surface, a colloidal crystal was prepared with the Langmuir-Blodgett (LB) technique. (ii) A polymer was deposited inside the colloidal crystal. (iii) Subsequent dissolution of this crystal resulted in fabrication of a macroporous film with a developed surface. In the resulting structure, the size of all macropores was the same and all of them were well interconnected. The applied procedure enabled a very precise control over macroporosity of the film. It was possible to tune pore diameter, film thickness, and the type of the structure (hollow spheres or inverse opals). The polymer film structures were examined using AFM and SEM. Moreover, electroanalytical (DPV) and spectroscopic (XPS, FTIR) characterization of the MIP films before and after template extraction enabled determination of efficiency of the template imprinting as well its subsequent extraction. Enantioslectivity of chemosensors for D- and L-arabitol was very high. Importantly, their LOD values were below the concentration of these analytes in urine of patients with disseminated candidiasis. All analytical parameters of chemosensors selective to HSA were excellent. That is, selectivity toward other protein interferences was high, LOD was at an impressively low femtomolar level of HAS concentration. Moreover, both sensitivity and stability of an analytical signal were high.