Abstract

The habilitation thesis "**Covalent Surface Functionalization with Aryldiazonium Salts: Applications in Electrochemical Sensors and Biosensors**" submitted by Assoc.Prof.Dr. Dimitrie-Matei-Damian RAICOPOL, presents the main scientific, professional and academic results of the candidate after obtaining his Ph.D. degree in 2012.

The first part of the thesis provides an overview of the candidate's academic and scientific achievements, including research projects, scientific papers, book chapters, conference presentations, and other relevant activities.

The second part of the thesis, which contains three chapters, highlights the most important scientific results obtained by the candidate in the field of covalent surface functionalization via electrochemical reduction of aryldiazonium salts.

Chapter II.1 describes a simple and efficient strategy for improving the overall selectivity of amperometric glucose biosensors, which employs aryl-modified platinum electrodes prepared using the electrochemical reduction of substituted aryldiazonium salts. The analytical applications of the modified electrodes are presented, and it is demonstrated that first- and second-generation interference-free glucose biosensors can be obtained by a judicious selection of the grafted layer at the platinum electrode substrate. The chapter also highlights an original approach for glucose biosensor fabrication, which involves the polymerization of pyrrole monomer in the presence of phenylsulfonyl-functionalized graphene, followed by surface modification with carboxyphenyl groups through the electrochemical reduction of the corresponding aryldiazonium salt. Grafting carboxyphenyl functionalities serves a dual purpose: it permits the covalent immobilization of glucose oxidase and forms a blocking layer which hinders the oxidation of interfering substances. The feasibility of this strategy is demonstrated by the preparation of a glucose biosensor which exhibited an improved performance in terms of linear range, sensitivity and selectivity towards common interferents.

Chapter II.2 outlines the possibility of fine-tuning DNA biorecognition interfaces by combining the significant advantages of surface grafting with silyl-protected aryldiazonium salts and "click" azide-alkyne functionalization reactions. Through this approach, the surface density of ssDNA aptamer bioreceptor molecules can be easily controlled by employing protecting groups of different sizes. The second part of the chapter presents an effective protocol for obtaining bifunctional monolayers with controlled composition. Specifically, if the "click" postfunctionalization is performed with a mixture of azide reagents, the surface composition of the mixed layer can be easily adjusted by controlling the mole ratio of the two azide-modified reagents in the "click" coupling solution. Such bifunctional layers containing ssDNA aptamer bioreceptor molecules and phosphorylcholine groups with antifouling

properties are able to effectively suppress non-specific protein adsorption and biofouling, while exhibiting sufficiently low impedance to enable electrochemical detection.

Chapter II.3 covers the synthesis and characterization of several thiosemicarbazone ligands bearing azido groups, which were immobilized on the surface of phenylethynyl-functionalized glassy carbon electrodes through a Cu(I)-catalyzed "click" reaction. Under optimized conditions and using the accumulation at open circuit-anodic stripping voltammetry technique, the ligand-modified electrodes exhibited a detection limit for Hg(II) in the nanomolar range, even in the presence of large amounts of interfering ions. The second part of the chapter describes a ferrocene-based thiosemicarbazone receptor which contains an intramolecular signalling pathway between the binding site and redox-active center. Notably, electrodes modified with the redox-active ligand allowed both the detection of Hg(II) ions by monitoring the potential of the ferrocene/ferrocenium redox couple using square-wave voltammetry, as well as their precise quantitation through anodic stripping voltammetry.

The third part of the thesis provides an overview of the candidate’s future research directions.