Amperometric Biosensors Based on Nanostructured Redox Polymer Thin Films

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We are currently developing chemistries that are potentially useful in the fabrication of biosensor arrays for use in diabetes management, during surgery, and in other clinical environments. Specifically, these amperometric sensors use oxidoreductase/redox polymer conjugates for molecular recognition and transduction, and use agents for the suppression of in vivo immune response such as poly(ethylene glycol) (PEG) and its derivatives. These components are then assembled to form nanostructured thin films, which we have shown can be used to form electrochemical sensor arrays very simply.

The first sensor fabrication scheme is based upon electrostatic complexation between the relevant sensor components. We initially functionalize an electrode (gold) surface with a negative surface charge by chemisorbing 11-mercaptoundecanoic acid. To this negative surface charge, we electrostatically bind a cationic osmium redox polymer. To the cationic redox polymer, we bind an anionic enzyme. This layer-by-layer assembly process may be repeated as desired for the generation of a multilayer structure, with the resultant nanostructures studied using ellipsometry, surface plasmon resonance spectroscopy and FTIR-external reflection spectroscopy. The studies reveled that these nanostructured thin films were structurally stable and that the secondary structure of the adsorbed proteins was preserved. Real-time SPR observations of film assembly indicated that both proteins and redox polymers rapidly adsorbed onto surfaces of opposing charge and that multi-component adsorption occurred, i.e. both the desired protein and contaminants in the protein preparation adhered to redox polymer surfaces. Combined SPR-cyclic voltammetry also suggested that these nanostructured films swell and shrink in response to changes in potential. Multilayer structures were further stabilized by chemical (exposure to glutaraldehyde) or photochemical (exposure to UV light in the presence of a photoinitiator) crosslinking. We also demonstrated patterning of these sensors using micro-contact printing or photolithography.

In addition to the multilayer structures, we are developing electroactive rod-coil block copolymers that form self-assembled, highly ordered films on electrode surfaces. Self-assembling redox polymers containing Os-based redox couples were produced by first synthesizing a polymerizable organometallic complex followed by the living anionic copolymerization of the redox monomer with isoprene or allyl amine. The living anion was then quenched to functionalize one terminus of the polymer and the “coil” segment of the polymer attached to a biphenyl ester “rod” composed of three hydroxyl biphenylcarboxylic acid segments. These materials were characterized by proton NMR, FTIR and gel permeation chromatography. Cyclic voltammetry experiments demonstrated rapid and reversible electrochemistry. When concentrated on an electrode surface, these rod-coil polymers tend to crystallize in the rod segment, forming nanostructured films with the rod nanocrystallite oriented to the electrode surface. Oxidoreductases may then be conjugated to these nanoassemblies via the isoprene or allyl amine moieties.