Title: DEVELOPMENT OF ENZYME-FREE HYDROGEN PEROXIDE BIOSENSOR USING CERIUM OXIDE AND MECHANISTIC STUDY USING IN-SITU SPECTRO-ELECTROCHEMISTRY

During recent development, it has been demonstrated that cerium oxide nanoparticles (CNPs) have exhibited catalytic activity which mimics naturally existing enzymes such as superoxide dismutase (SOD) and catalase. The underlying mechanism is attributed to the modulation of oxygen vacancies on CNPs lattice by dynamic switching of the oxidation states between Ce3+ and Ce4+ due to the electron transfer resulting from the redox reaction between CNPs and reactive oxygen species such as hydrogen peroxide (H2O2). Thereby the redox potential of CNPs is dependent on the surface chemistry i.e. the surface concentration of Ce3+ and Ce4+. Currently, the ratio of Ce3+/Ce4+ in CNPs is characterized ex-situ using XPS or TEM which involves sample drying and exposure to high energy X-rays and electron beam, respectively. Sample drying and high energy beam exposure could lead to sample deterioration. The goal of the study is to explore a technique to characterize CNPs in-situ and identify the surface chemistry of CNPs. The in-situ investigation of CNPs was carried using spectroelectrochemistry wherein the electrochemical and optical measurements are carried out simultaneously. Detailed optical characterization of two different CNPs having different catalytic activity were carried under oxidation and reduction environments. Analysis of spectra revealed widely different redox potential for CNPs which was a function of pH and composition of buffer solution.

In second part of dissertation a suitable surface chemistry of CNPs is investigated to replace the enzyme in biosensor assembly to allow amperometric detection of H2O2 in physiological conditions. Upon electrochemical investigation of the physiochemical properties of CNPs, it was found that CNPs having higher surface concentration of Ce4+ as compared to Ce3+ oxidation states, demonstrated increased catalytic activity towards H2O2. The addition of CNPs resulted in 5 orders of increment in amperometric current with a response time of 400 msec towards detection of H2O2 and exhibited excellent selectivity in presence of interfering species. Additionally, cerium oxide was successfully integrated into the biosensor assembly through the anodic electrodeposition, which allowed the transfer of electron generated from the CNPs in the redox reaction to the electrode and demonstrated successful sensing of H2O2. Furthermore, to achieve detection of H2O2 in physiological conditions, CNPs were integrated with nanoporous gold (NPG) which exhibited anti-biofouling properties. The anti-biofouling property of NPG was investigated using electrochemical techniques and showed excellent signal retention in physiological concentration of albumin proteins. The novel study targets at developing robust enzyme free biosensor by integrating the detection ability of CNPs with the anti-biofouling activity of NPG based electrode.

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The public is welcome to attend.