



**COLLEGE OF ENGINEERING
AND COMPUTER SCIENCE**

FINAL ORAL EXAMINATION

OF

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BS, Indian Institute of Technology, Kharagpur, India, 2010

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DOCTOR OF PHILOSOPHY
IN MATERIALS SCIENCE AND ENGINEERING

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DISSERTATION RESEARCH IMPACT

I have developed an in-situ methodology to characterize cerium oxide nanoparticles using spectroelectrochemistry without any damage from high energy beam as used in other techniques. Additionally it utilizes simple instrumentation and cuts down the cost and time for characterization. The methodology has a huge potential for quality testing of nanoparticles and has direct applications in semiconductor and biosensor industries. In second part of dissertation, an enzyme free biosensor for hydrogen peroxide (H₂O₂) is developed using cerium oxide nanoparticles assembled on nanoporous gold platform. The inorganic metal oxide nanoparticle resulted in a robust biosensor which overcame issues from the enzyme based biosensor. Additionally, nanoporous gold allowed continuous sensing in biofouling environment. This biosensor is a major upgrade from the currently used commercial biosensor due to its robustness and excellent detection in biofouling conditions.

SELECTED PUBLICATIONS & PATENTS

The induction of angiogenesis by cerium oxide nanoparticles through the modulation of oxygen in intracellular environments, S. Das, S. Singh, J.M. Dowding, S. Oommen, A. Kumar, T.H.XT Sayle, S. Saraf, & S. Seal, in Biomaterials, 2012.

Fabricated Micro-Nano Devices for In vivo and In vitro Biomedical Applications, S. Barkam, S. Saraf, & S. Seal, in Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology , 2013.

Understanding the adsorption of polyelectrolyte coating on redox active nanoparticles using soft particle electrokinetics, S. Saraf, C. Neal, S. Das, S. Barkam, & S. Seal, in ACS Applied Materials and Interfaces , 2014.

Electrochemical study of nanoporous gold revealing anti-biofouling properties, . S. Saraf, C. Neal, S. Park, S. Das, S. Barkam, H.J. Cho, & S. Seal, in RSC Advances , 2015.

Self-Assembly of PEG-coated Ceria Nanoparticles shows dependence on PEG Molecular weight and Ageing, C. Neal, S. Das, S. Saraf, & S. Seal., in ChemPlusChem , 2015.

The Change in Antioxidant properties of Dextran Coated Redox Active Nanoparticles due to Synergetic Photo-reduction-oxidation, S. Barkam, S. Das, S. Saraf, & S. Seal. , in Chemistry - A European Journal , 2015.

Ionic Conductivity of Bias Sputtered Lithium Phosphorus Oxynitride Thin Films, P. Mani, S. Saraf, V. Singh, M. R. Robert, A. Vijayakumar, S. J. Duranceau, S. Seal & K. R. Coffey, in Solid State Ionics, 2016.

Patents:

Thermal Spray of Repair and Protective Coatings, 62/139,006

DISSERTATION

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 Ce^{3+} and Ce^{4+} due to the electron transfer resulting from the redox reaction between CNPs and reactive oxygen species such as hydrogen peroxide (H_2O_2). Thereby the redox potential of CNPs is dependent on the surface chemistry i.e. the surface concentration of Ce^{3+} and Ce^{4+} . Currently, the ratio of $\text{Ce}^{3+}/\text{Ce}^{4+}$ 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 H_2O_2 in physiological conditions. Upon electrochemical investigation of the physio-chemical properties of CNPs, it was found that CNPs having higher surface concentration of Ce^{4+} as compared to Ce^{3+} oxidation states, demonstrated increased catalytic activity towards H_2O_2 . The addition of CNPs resulted in 5 orders of increment in amperometric current with a response time of 400 msec towards detection of H_2O_2 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 H_2O_2 . Furthermore, to achieve detection of H_2O_2 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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SELECTED AWARDS & HONORS:

2010, UCF Graduate Dean's Fellowship

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