Reactive oxygen species (ROS) are byproducts of physiological processes. Strengthened production of ROS is known to cause acute conditions such as inflammation, aging, Alzheimer's disease, melanoma and ovarian cancer, fibrosis and multiple sclerosis. Therefore, early detection of ROS at nanomolar concentration (at cellular level) and developing more potent antioxidants is essential for regular health monitoring and early stage treatments. Inflammation is also triggered by wear debris in orthopedic implants resulting in revision surgery. Coatings of redox-active materials on implants have potential to mitigate the inflammation and delay the need of revision surgery. This dissertation focus on developing advanced functional nanomaterials by tailoring the surface chemistry of existing materials. Surface chemistry of materials can be altered by introducing defects in the lattice structure. Three materials system, doped cerium oxide nanoparticles (d-CNPs), cerium oxide thin films (CeOx) and molybdenum disulfide (MoS2) nanoparticles, have been studied for its potential biomedical and biosensing applications.

Surface Ce3+/Ce4+ oxidation state in CNPs controls the bio-catalytic activity. Higher superoxide dismutase (SOD) is demonstrated by high Ce3+/Ce4+ oxidation state. On the other hand, improved catalase mimetic activity is observed for low Ce3+/Ce4+ CNPs. Different CNPs preparation results in different Ce3+ to Ce4+ ratio, particle size, surface coating, and agglomeration, thus significantly varying the antioxidant properties of CNPs. In the first section of the dissertation, sustainable one-step room temperature synthesis of rare earth element (La, Sm, and Er) d-CNPs have been developed to effectively control the Ce3+ to Ce4+ ratio for specific biological application. Substitution of Ce4+ ions by trivalent dopants from ceria lattice increases the oxygen vacancies and density of catalytic sites. Uniform distribution of trivalent dopant in ceria lattice confirmed by EFTEM is attributed to enhanced SOD mimetic activity, ROS scavenging and tuning surface Ce3+/Ce4+ oxidation state in CNPs. Surface chemistry of atomic layer deposited (ALD) CeOx thin films have also been tailored by controlling the film thickness. CeOx film of 2 nm thickness has high Ce3+/Ce4+ (ratio 1) whereas higher thickness films (6-33 nm) have lower Ce3+/Ce4+ (ratio 0.30-0.37). These films have been further tested for catalase mimetic activity and hydrogen peroxide (H2O2) detection.

Ascorbic acid, found in the biological system, interfere in the electrochemical detection of H2O2 resulting in poor selectivity of cerium oxide based sensors. To improve the selectivity of electrochemical sensors, Sulfur-deficient redox-active MoS2 have been utilized for electrochemical detection of pharmaceutically relevant chemical species. S-deficient MoS2 nanoparticles have been prepared by liquid exfoliation method to increase Mo-edge density and tested as sensing materials for detection of pharmaceutically relevant H2O2, hypochlorous acid (HOCl) and reactive nitrogen (NO*) species. Addition of ascorbic acid and uric acid have shown no interference during H2O2 detection. Change in S to Mo ratio have been studied using x-ray photoelectron spectroscopy. Density functional theory (DFT) have been employed to understand the detection mechanism and size-dependent sensitivity of MoS2. DFT study further reveals the role of S-deficiency and Mo- and S-edges in the higher catalytic activity of 5-7 nm MoS2 particles. Through these studies, the importance of defects in nanomaterials and their exotic properties at the nanoscale have been demonstrated. Understanding developed from these studies have provided the framework to develop more advanced functional nanomaterials for biomedical and biosensing applications.
Sudipta Seal, Chair, Materials Science and Engineering
Hyoung Jin Cho, Materials Science and Engineering
Yajie Dong, Materials Science and Engineering
Alfons Schulte, Department of Physics
Lei Zhai, Materials Science and Engineering

Approved for distribution by Sudipta Seal, Committee Chair, on April 23, 2017.

The public is welcome to attend.