

395e Nano-Structured Diamond Surfaces for Electrochemical Sensing Applications

Scott Wolter

Diamond has many fundamental benefits as the working electrode in electrochemical sensors. It is chemically and mechanically robust, characterized by a wide potential range for water electrolysis, maintains its functionalized surface through multiple cycles and is resistant to fouling. The potential range for water stability is limited in conventional metallic and glassy carbon working electrodes and, consequently, inhibits the detection of certain electrochemical reactions, an important consideration in sensor applications. Anodic potentials applied to diamond electrodes far exceed conventional electrodes and are comparable, but more environmentally friendly, to Hg-electrodes under cathodic potentials, which are used for trace metal detection. Current challenges facing electrochemical sensors include the development of sensors with increased selectivity to environmentally important chemical species. Furthermore, their lifetime and robustness must be enhanced so that they can function in field environments. Diamond is an excellent transduction platform to address these challenges by virtue of its outstanding electrochemical properties and the robust, established chemistries for covalent functionalization of carbon surfaces. We present research targeting diamond working electrodes in electrochemical sensors. Polycrystalline boron-doped and undoped films were grown using microwave plasma chemical vapor deposition for this effort. The sensors comprise diamond functionalized with alkyl linking groups tethered to molecules intended to be responsive to target analytes. The primary amine group of the modified diamond surface is exposed and can undergo peptide bond formation with amino acid receptors. Candidate amino acids, namely cysteine, tyrosine, glutamate, and glutamine (or their modified chemical forms such as glutathione) have been targeted for their potential sensitivity to nitrate ions. In particular, cysteine has been shown to be responsive to NO species, similar to tyrosine, in studies involving biological processes. Generally, NO_x species are relevant to immune, antimicrobial, smooth tissue relaxant, and neuronal bioactivities, and clues may be garnered from these processes for the design of biomimetic sensors. An important consideration, and an initial focus of our work, is the affect of the functional groups on the potential window of water stability and the integrity of the chemical groups under extreme operating potentials. Another consideration is the dipolar attributes of the functional groups. While potentiometric measurements indicate specific redox potentials for the target analytes, an alteration in the functional group dipole moment upon interaction (binding) with the analyte is expected to affect the surface double-layer capacitance. Such effects have been evaluated through impedance measurements and modeled from conventional Nyquist and Bode plots. Although specific functional groups have been explored and utilized to bind specific nitrate ions, a broader understanding of these reactions provide insight into how the chemical nature of the diamond surface in its functionalized and un-functionalized state affect chemical sensing and stability.