Synthesis, Electrochemistry, and Surface Functionalization of Nitrogen-doped Ultrananocrystalline Diamond. J.A. Carlisle, J. Wang, O. Auciello, and M.A. Firestone

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Diamond offers several potential advantages as a platform material for bioinorganic interfaces, including chemical & bio-inertness, electrochemistry, and tunable hydrophobicity. Ultrananocrystalline diamond (UNCD), with a unique combination of physical, chemical and electrical properties, is well suited for a variety of biochemical/biomedical applications such as hermetic coatings, MEMS compatible biosensors, implants, and bioelectrodes. UNCD can be deposited at temperatures as low as ~400 °C, and nitrogen-doped UNCD thin films that are synthesized using argon-rich Ar/CH₄/N₂ plasmas, can have room temperature conductivities as high as 250 Ω^{-1} cm⁻¹, and have unique electrochemical properties. Surface functionalization of these films could enable their use as electrochemical bioinorganic interfaces.

Over the past two years we have worked to develop UNCD surface functionalization strategies, e.g. photochemical and electrochemical procedures, which enable control of hydrophobicity and biochemistry, thereby promoting the selective absorption of biomolecules and the suppression of biofouling. We have demonstrated that the electrochemical reduction of aryl diazonium salts leads to a covalently bonded organic layer on the surface of conducting UNCD thin films. The surface layer was observed and characterized by X-ray photoelectron spectroscopy, contact angle measurements, cyclic voltammetry and ac impedance measurements. The surface coverage of tethered aryl derivatives is as high as 70% of a compact monolayer. The organic layer is very stable, and is decomposed only at temperature above 600 °C when heated in an ultrahigh vacuum. By choosing different aryl derivatives we are also able to tune the surface properties of UNCD such as its surface hydrophobicity and reactivity. Covalently bonded phenols should also support electron transport more readily than other chemistries. Amine-terminated phenol groups should serve nicely for the attachment of a wide variety of linker molecules that have been extensively studied previously. Thus, we envision this new diamond functionalization technique as enabling a new immobilization chemistry that will permit modification of UNCD and other diamond surfaces to construct an entirely new class of bio-inorganic interfaces based on diamond thin films.