Electrochemical Functionalization of Ultrananocrystalline Diamond (UNCD)

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Motivations

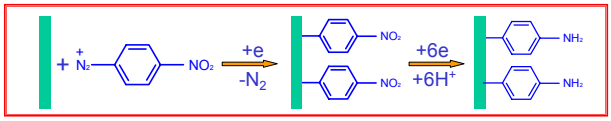
- Silicon-based biodevices are greatly limited due to inability to effectively interface with biological milieu in non-immunogenic and stable manner.
- UNCD exhibits unique combination of physical, chemical,electrical and biocompatible properties well suited for a variety of applications such as MEMS chemical sensors, chip-based biosensors, implants, and bioelectrodes.
- Control of interactions between biomolecules and the UNCD surface is critical.
- This project is focused on investigating UNCD surface functionalization strategies (e.g. photochemical and electro-chemical procedures) that enable control of UNCD surface hydrophobicity and charges, thereby promoting the selective absorption of biomolecules, and the suppression of biofouling.
- The integration of biological functions with UNCD will ultimately yield robust UNCD-based biosensors for high-throughout detection applications, including biological weapons agents, environmental biohazards, DNA diagnostics, and drug discovery.

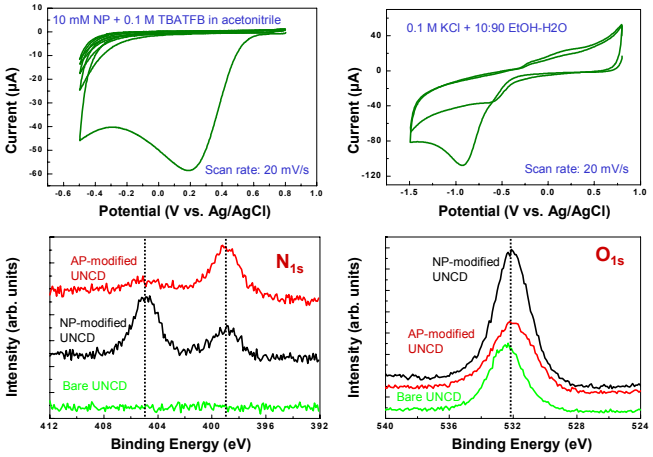
Scientific Achievement

- Functionalization of conductive (N-doped) UNCD films can be achieved by electrochemically reducing aryl diazonium cations in a nonaqueous medium
- One-electron transfer reaction leads to the formation of solution-based aryl radicals that couple to the UNCD surface, forming covalent C-C bonds.
- Modified UNCD surfaces were fully characterized by AFM, XPS, NEXAFS, cyclic voltammetry and impedance measurements.
- XPS spectra show chlorine or nitrogen signals after 3, 5-dichlorophenyl or 4-nitrophenyl groups were attached to the UNCD surface. The surface coverage, estimated from the electrochemical and XPS measurements, is as high as 70% of a compact monolayer.
- Facile electron transfer to redox active groups attached to UNCD surfaces via aryl derivatives observed by cyclic voltammetry and AC impedance measurements. The attached aryl derivatives served as conductive linker for subsequent attachment of a variety of biomolecules.

Surface Functionalization of UNCD

(4-nitrophenyl diazonium)

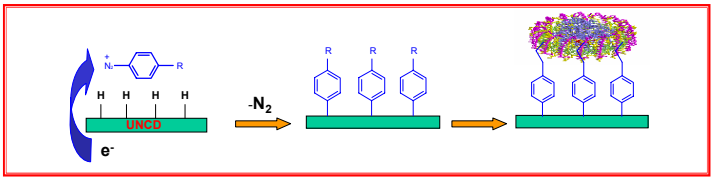




- XPS spectra confirmed the attachment of nitro group (NO_2) and its transformation to amine group (NH_2). The O/C ratio is increased from 7% (bare UNCD) to 18% after NP was grafted at UNCD surface, and then reduced to 11% after the NO_2 was transformed to NH_2.

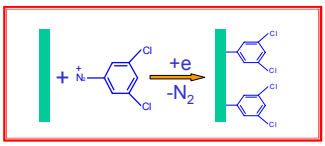
Electrochemical Functionalization of UNCD Surface

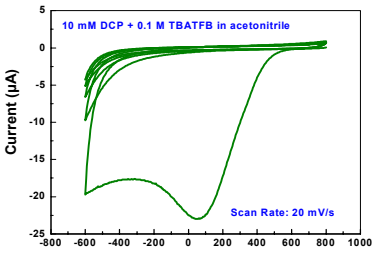
Solution-based aryl radicals, generated by electrochemical reduction of diazonium salt, couple to UNCD surface forming covalent C–C bonds. The attached aryl derivatives serve as a linker for the subsequent attachment of biomolecules.

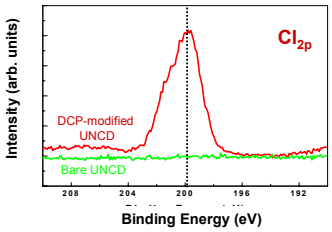


Surface Functionalization of UNCD

(3, 5-dichlorophenyl diazonium)



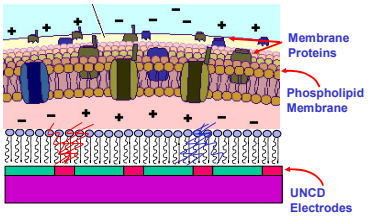




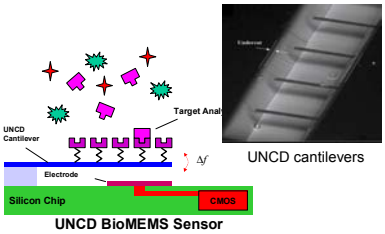
- XPS spectra confirm the attachment of DCP to UNCD surface. The Cl/C ratio is about 14%.
- The DCP-modified UNCD surface is hydrophobic.

Future Work: Functionalized UNCD Interfacing with Biomaterials

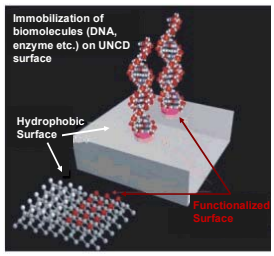
- **UNCD/proteo-complex fluids composites for energy transduction**
  - Fundamental understanding of biomolecule/inorganic interfaces
  - Investigation of energy transport and electron transfer processes



- **UNCD bioMEMS sensor**
  - UNCD can be grown at low temperatures
  - UNCD Mechanical properties (high frequency, high Q)
  - UNCD MEMS
  - Biocompatible, chemically inert
  - Tunable surface — hydrophobicity



- **UNCD-based electrochemical biosensors**
  - Enzyme-modified electrodes
  - DNA sensors
  - Immunosensors
  - Advantages of UNCD electrochemical sensor
    - Long life time
    - Light-weight, portable
    - Extremely sensitive



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