Reduction-Oxidation reaction of adsorbed quinone at a graphitic surface

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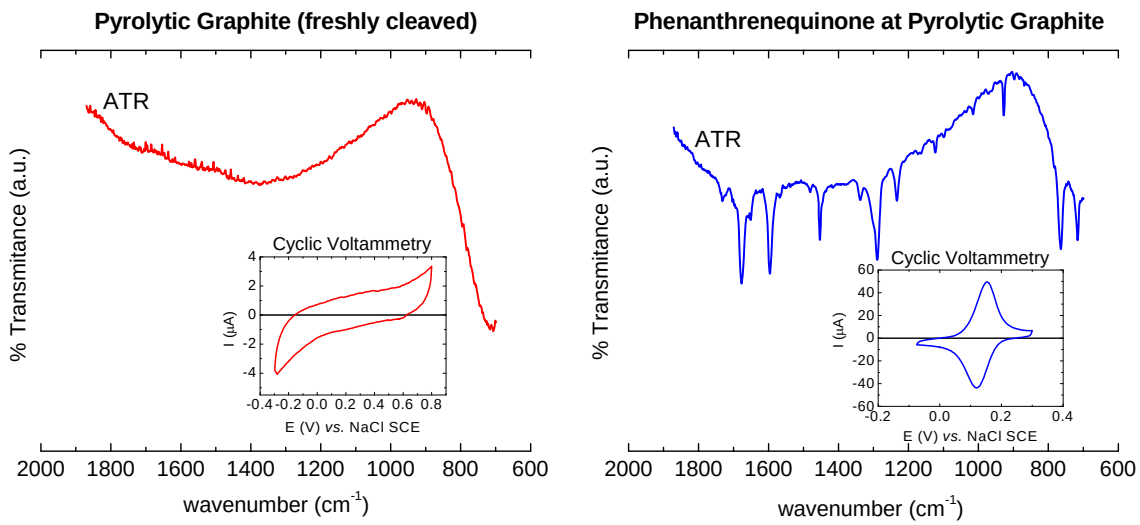
Thrust 3: Catalytic Reactions at Fluid/Solid Interfaces

Understanding multi-electron transfer reactions at a fluid solid interface is crucial for controlling these reactions at electrode and electro-catalytic surfaces. We hypothesize that multi-electron reactions may occur by a sequence of proton-coupled electron transfer reaction steps and our approach is to probe how a model red-ox reaction occurs and is related to adsorption of redox molecules and proton donors at the fluid-solid interface. As an initial step we will probe the reaction rate of the reversible reduction-oxidation of quinones adsorbed at graphitic carbon surfaces.



We have now correlated cyclic voltammetry with surface infrared spectroscopy of 9,10-phenathrenequinone (PQ). PQ was deposited on a freshly cleaved basal plane surface of pyrolytic graphite (PG) by exposing the graphite to a dilute precursor solution of PQ. Exposure to PQ was followed by careful rinsing to remove multi-layer excess PQ. The graphite surface was measured by ATR-FTIR before and after exposure. The appearance of strong quinone IR features proved the strong adsorption of a near monolayer surface concentration of PQ on the graphite surface. Corresponding cyclic voltammograms performed in hydrochloric or perchloric acid showed that exposure to the PQ (and rinsing) led to the appearance of red-ox response of the surface, yielding anodic and cathodic features at 0.14 and 0.11 V, respectively, indicating that the response is correlated with the surface adsorbed PQ. Work is in progress to quantify the rates of this red-ox process, by parametric variation of sweep rates, in both H_2O and D_2O to look for an isotopic effect that would implicate that solvent mediated coupled proton-electron transfer is controlling the reaction rate.