The Electrochemistry of Catalyzed Metal Multilayers

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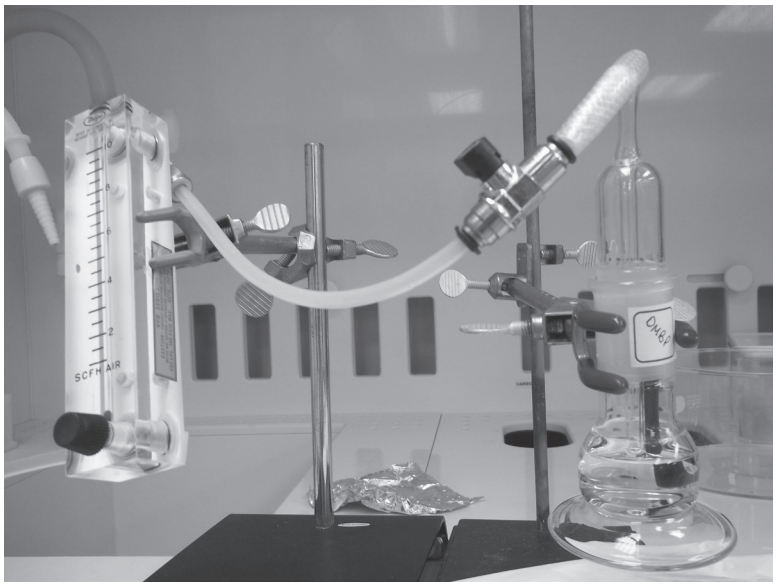

Figure 1: Research setup.

Abstract:

Self-assembled multilayers (SAM) are a product of the bottom-up fabrication method, a technique in which substances are built from the molecular level through chemical reactions. With thoughtful manipulation, such fabrications could perform as numerous components in molecular devices. This project utilized the bottom-up method to produce multilayers of the 4,'4 dimercaptobiphenyl (DMBP) attached to the group (II) B metal mercury (Hg). The focus was to analyze its electrochemical properties by cyclic voltammetry to determine if the structure could successfully conduct electrons. A current of potential energy was ramped up and inverted through the sample and the oxidation state of the mercury was analyzed. This reading concluded if mercury was being reduced. Currently a peak occurred around the potential 0.4 V when a monolayer of DMBP was capped with mercury, but the peak did not occur when bonded with a second DMBP. Trials are being conducted for confirmation of current data, to determine if multiple oxidation states of mercury are present, and provide understanding of other chemical properties of the substance.

Preparation of Multilayers:

The initial monolayer was prepared by introducing a gold working electrode to a 1 μM DMBP solution with 200 proof ethanol. The gold working electrode, with a disk diameter of 1.6 mm, was placed into the monolayer solution in a nitrogen atmosphere for three hours, as seen in the setup in Figure 1. The electrode was then rinsed off with ethanol and dried with a nitrogen jet gun. Mercury was introduced to the monolayer via a dilute solution of 0.008M mercury perchlorate ($Hg(ClO_4)_2 \cdot (6H_2O)$) and 200 proof ethanol. The electrode was again positioned in the solution for three hours with nitrogen, thoroughly washed with distilled water and ethanol, and then dried off with nitrogen. The gold electrode was alternatively introduced to the monolayer and mercury solution, creating DMBP and mercury multilayer. A cartoon of the assembled structure is shown in Figure 2. After every layer, cyclic voltammetry was performed to measure the sample's electrochemistry.

Cyclic Voltammetry:

Cyclic voltammetry determines the electrochemical properties of a sample through a series of cathodic and anodic measurements. For this experiment, our general setup included three electrodes enclosed in a glass cell partially filled with a 0.1 M sodium perchlorate electrolyte solution. The gold electrode served as the substrate for the various monolayers formed. Its potential energy was ramped up to a maximum current of 600 mV, then inverted to a set minimum of -600 mV, scanning the sample for two sweeps and six sweeps. The known electrochemical behavior of the silver/silver chloride electrode was used as a reference to measure the potential energy of the working electrode. A platinum counter electrode maintained a stable environment for oxidation and reduction.

Results:

Two attempts were completed. In the first attempt, five layers were made, three being the DMBP monolayer and two being Hg. Cyclic voltammetry of the first layer showed few peaks,

however as we continued building layers, a gradual increase in cathodic and anodic peaks occurred. Unfortunately, in the first attempt, we failed to eliminate oxygen as a factor in the experiment. We noticed this because of some peaks that were present that we could not attribute solely to the expected chemical reaction. We alleviated this problem in our second attempt by degassing the entire cell for 10 minutes prior to measuring the electrochemistry of the sample. During the second trial, we grew a total of three layers, two DMBP monolayers amid one layer of Hg. The sample with just the DMBP layer had very little peaks, similar to the results in the previous trial. The trial pertaining to the DMBP monolayer capped with a layer of Hg had two cathodic peaks, appearing around potential values of 500 mV and -200 mV. The same sample also had one anodic peak at an approximate potential value of -130 mV. Once another layer of DMBP was assembled on top of the DMBP and Hg layers, the cyclic voltammetry showed similar occurrences of very little peaks. Graphs of both attempts are depicted in Figure 1 and Figure 3.

Conclusions:

The occurrence of the anodic and cathodic peaks discussed previously indicates a significant change in the chemical behavior of the sample, suggesting successful formations of the DMBP and Hg multilayers. The sample capped with DMBP showed very few peaks, correlating with our expectations. At this state, Hg is not exposed to the electrolyte solution and there is no free electron available to react with the Hg. Future works would include continuing further trials on DMBP and Hg multilayers, and replacing DMBP with other organic molecules.

Acknowledgements

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References:

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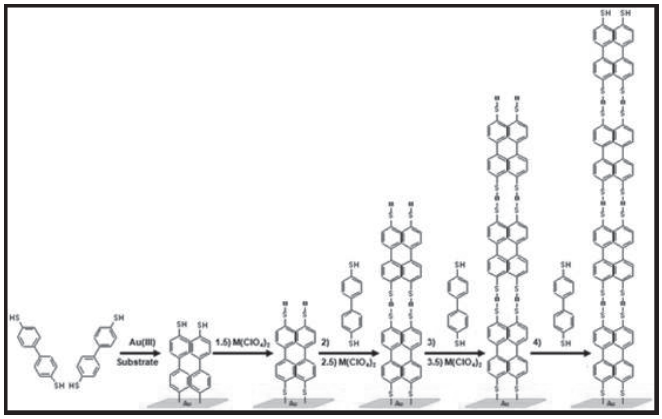

Figure 2: Multilayers of DMBP and Hg on gold substrate.

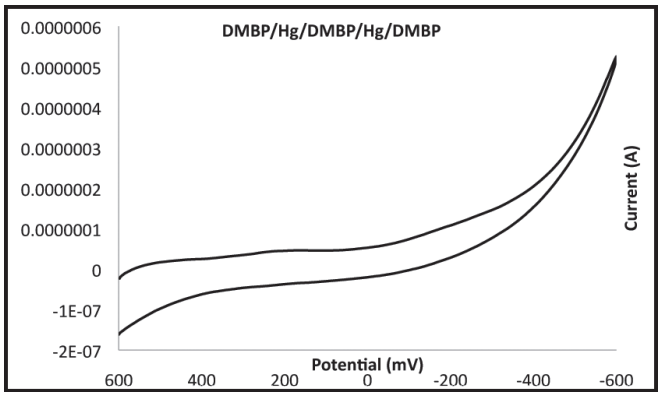

Figure 3: Cyclic voltammetry of first attempt with three DMBP monolayers and two layers of Hg.

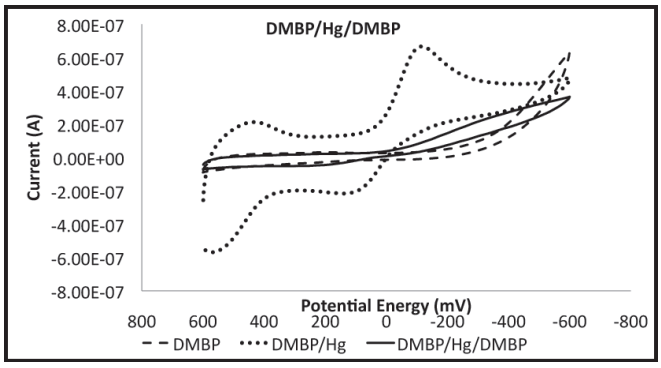

Figure 4: Cyclic voltammetry of second attempt with two DMBP monolayers amid a layer of Hg.