Defect Analysis of Molecular Monolayers with Electrochemistry

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Introduction:

Self-assembled monolayers (SAMs) can be formed on metal surfaces to modify the surface and control the properties of interfaces [1]. Although the electronic properties of alkanethiols have been extensively studied over the years and have been shown to form well ordered and closely packed SAMs [2], oligopeptides have not been as prevalent in SAM studies. Therefore, we electrically characterized oligopeptides of varying lengths with drop electrode experiments to study the electron transfer through the monolayer in fluid gallium indium eutectic and gold electrode junctions.

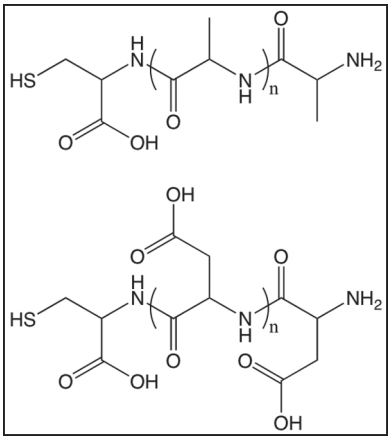

Figure 1: Structures of investigated oligopeptides.

The oligopeptides showed tunneling current-voltage (I-V) curves, but histograms displayed a broad range of current densities per oligopeptide, indicating that the molecular layer was not defect free. Even though oligopeptides may have better order in comparison to other molecules, their ordering is not sufficient for these junctions. This finding motivated further research into monolayer formation and defects.

Electrochemistry and cyclic voltammetry are powerful methods to explore the processes in metal electrode interfaces. The reduction and oxidation reactions that occur at the surface produce electrical currents, which provide information about the order and density of the SAM. If the monolayer were ordered and closely packed, redox molecules would be blocked by the monolayer and could not exchange electrons with the metal surface. Redox behavior can give insight to molecular defects and pinholes.

Experimental Procedure:

Materials. The oligopeptides used in this study had the following sequences: Cys-$(Ala)_n$-Ala and Cys-$(Asp)_n$-Asp, where *n* ranged from 2-5 (Figure 1). The peptides were purchased from Caslo Laboratory (Lyngby, Denmark) with purity greater than 95%. One millimolar (mM) peptide solutions in Milli-Q grade water were prepared and stored at 4°C. Lithium perchlorate ($LiClO_4$), potassium hexacyanoferrate(II) ($K_4Fe(CN)_6$), sodium hydroxide (NaOH), and perchloric acid ($HClO_4$) solutions were prepared with Milli-Q grade water and stored at room temperature.

SAM Preparation. 100 nm gold (Au) substrates were prepared via electron beam physical vapor deposition on a 400 nm silicin oxide (SiO_2) insulating layer and a 10 nm titanium (Ti) adhesion layer on Si. The Au substrates were cleaned with isopropanol and then O_2 plasma for three minutes to remove organics on the surface. A 50 μl peptide solution was placed on top of the clean substrate for at least 72 hours. The modified substrates were finally rinsed with water and dried with nitrogen gas before testing.

Electrochemistry Measurements. A 3-electrode compression cell was used, with a modified Au substrate working electrode, standard calomel reference electrode (SCE), and platinum wire counter electrode. We then exposed 0.32 cm^2 of the modified Au substrate to the electrolyte solution. Cyclic voltammograms started at 0.0 V, swept to -0.1 V, +0.45 V, and then back to 0.0 V. Scans were repeated twice before the third scan was recorded, at a scan rate of 25 mV/s. For each modified Au substrate, measurements were first performed with increasing electrolyte concentration (5, 25, 50, 75, and 100 mM $LiClO_4$), then with 5 mM $HClO_4$, and finally with 100 mM NaOH, all using 2.5 mM $K_4Fe(CN)_6$ as the redox molecule. The electrochemical cell system was rinsed with water three times and allowed to cycle with pure electrolyte before each recording.

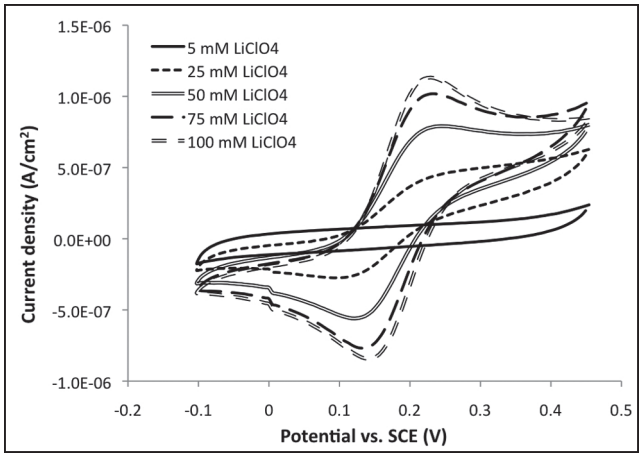

Figure 2: Cyclic voltammograms of Cys-Ala-Ala-Ala SAM on Au.

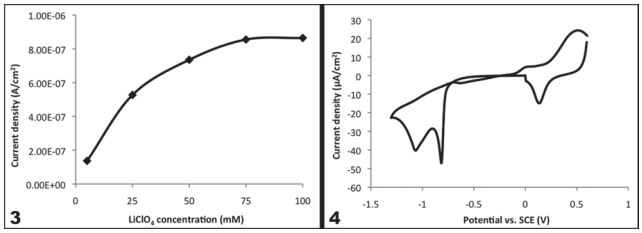

Figure 3, left: Cys-Ala-Ala-Ala SAM on gold, plotted at 0.35 V.

Figure 4, right: Desorption of Cys-Ala-Ala-Ala SAM on gold.

Results and Discussion:

In electrochemistry measurements, the $Fe(CN)_6$ redox response of Au substrates coated with oligopeptide SAMs was investigated. At 5 mM $LiClO_4$ electrolyte concentration, no redox behavior was observed. However, increasing the electrolyte concentration revealed increasing redox behavior (Figure 2). This trend, seen with all peptide monolayers, is due to the decrease of the effective diameter of the redox molecules. As the electrolyte concentration increases, the redox molecules are less hydrated and have a smaller solvent cage surrounding them. Since the size of the pinholes and defects remain constant for each sample, more redox molecules can access the gold layer when their effective diameters are smaller. This effect can change the current density up to one order of magnitude between the lowest and highest concentrations of $LiClO_4$.

The increase in current density with electrolyte concentration for the Cys-Ala-Ala-Ala SAM can be seen in Figure 3. Although not all peptide SAMs display the same threshold shape curve, they all have a positive correlation between current density and electrolyte concentration.

Potential induced desorption peaks are another indication of monolayer defects. These cyclic voltammograms are recorded with 100 mM NaOH, and swept from 0.0 V, -1.3V, +0.6V, to 0.0 V. Only the first scan was recorded.

The Cys-Ala-Ala-Ala SAM desorption is shown in Figure 4. The sharpest peak, the desorption peak of the monolayer, occurs at -0.81V. If the monolayer contained no defects, this desorption peak would be the only peak between -1.3V and 0.0 V. However, a broader peak at -1.06V is also present, which indicates that there are domains that desorbs at more negative potentials. This behavior is seen with all peptide SAMs.

Conclusion:

Defects of peptide SAMs on gold were investigated with electrochemistry. Pinholes were discovered by changing the electrolyte strength, thereby changing the effective diameter of the redox molecules. Redox molecules larger than the pinhole diameter were blocked by the monolayer and could not exchange electrons with the underlying gold substrate. The effects of gold substrate roughness, peptide length, and potential of hydrogen (pH) were also analyzed for the peptide monolayers (data not shown).

Although these results give insight to monolayer defects using electrochemistry, further experimentation is necessary to fully understand whether these peptide monolayers can truly form defect-free and closely packed SAMs.

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References:

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