

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.

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

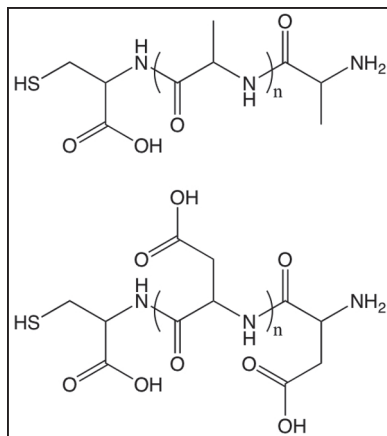


Figure 1: Structures of investigated oligopeptides.

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 (LiClO₄), potassium hexacyanoferrate(II) (K₄Fe(CN)₆), sodium hydroxide (NaOH), and perchloric acid (HClO₄) 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 silicon oxide (SiO₂) insulating layer and a 10 nm titanium (Ti) adhesion layer on Si. The Au substrates

were cleaned with isopropanol and then O₂ plasma for three minutes to remove organics on the surface. A 50 μ l 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 cm² 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 LiClO₄), then with 5 mM HClO₄, and finally with 100 mM NaOH, all using 2.5 mM K₄Fe(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.

