Quantifying lateral interactions in gold self-assembled monolayers: The effect of topography and surface concentration

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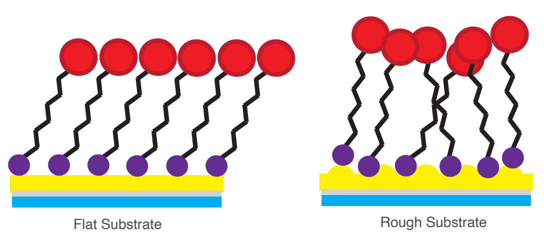
Background

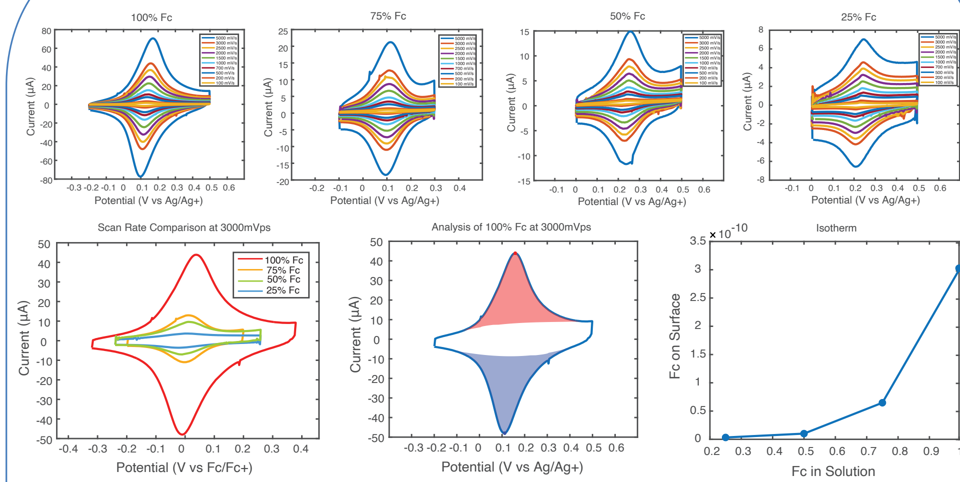
Lateral interactions are van der Waal forces regarding electrostatic repulsions or attractions between molecules. Through increased surface loading, molecules experience more repulsive forces and negative lateral interactions and through decreased surface loading, molecules experience more attractive forces and positive lateral interactions. We are able to assess the lateral interactions between the electroactive ferrocene (Fc) headgroups in self-assembled monolayers (SAMs). SAMs of alkanethiols on gold are well-ordered structures with ideal electron transfer kinetics and ferrocene is a stable and extensively studied redox probe.

Goal: Quantify lateral interactions between electroactive molecules attached to gold surfaces of increasing roughness and varying surface concentrations of ferrocene in mixed monolayers.

Hypothesis: As roughness increases, there will be more negative and repulsive lateral interactions between ferrocene molecules.



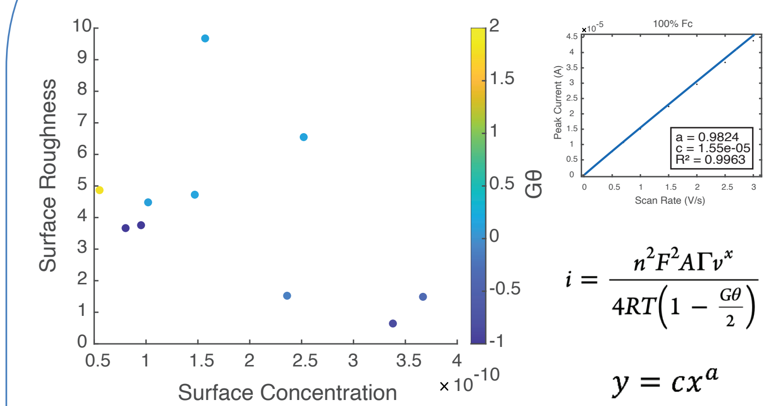
Surface Concentration



$$concentration\ of\ Fc = \frac{moles\ of\ Fc}{area\ of\ electrode\ (cm^2)}$$

- Concentration of ferrocene can be calculated by integrating the area underneath the anodic/cathodic curve

Lateral Interactions



$$i = \frac{n^2F^2A\Gamma v^x}{4RT\left(1-\frac{G\theta}{2}\right)}$$

$$y = cx^a$$

- Usage of Laviron's equation to calculate Gθ or lateral interactions
- More negative Gθ values indicate repulsive forces between ferrocene molecules
- With increased roughness and surface loading, there are more negative Gθ values, which indicate repulsive forces between ferrocene molecules
- Positive Gθ values are present at high roughness because of low surface coverage on the electrode

Methods

- Gold electrodes were prepared using a template stripping method where the template topographies were changed with a two-step process of metal-assisted chemical etching (MACE) using HF/H_2O_2

1) Different methods in the 1st step of MACE technique
   A. Soak silicon in poly-L-lysine and then gold nanoparticles to attach varying sized gold nanoparticles on the surface
   B. Soak silicon in HF/AgNO3 solution to deposit Ag nanoparticles on the surface, then varying etching times
2) Gold was deposited onto modified silicon wafer using electron beam evaporation
3) Glass pieces were attached to gold using epoxy, cured under UV light, and removed

- Electrodes are then immersed in mixtures containing different ratios of 6-(ferrocenyl)hexanethiol and 1-hexanethiol to result in monolayers of different surface concentrations of ferrocene
- Cyclic voltammetry is used to determine surface concentration and lateral interactions of ferrocene
- Atomic force microscopy (AFM) is used to measure surface roughness of the gold electrodes

Template Stripping Process

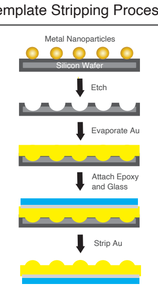
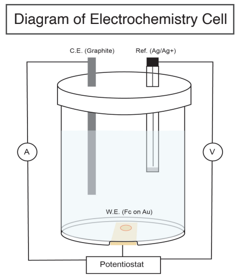
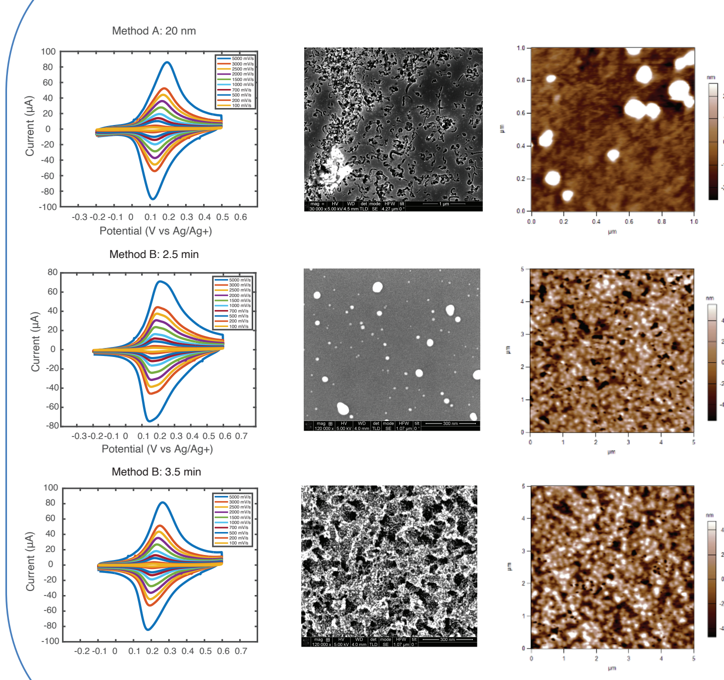


Diagram of Electrochemistry Cell



Exposure to HF can be fatal and H_2O_2 reacts violently with organics, so care must be taken when handling these chemicals. We always used the smallest volume necessary for our samples and all steps involving these chemicals were carried out by T. Teitsworth (a postdoctoral researcher) who wore an apron, face-shield, and gloves.

Roughness



- RMS: 5.195 ± 2.5 nm
- SEM imaging of 20 nm nanoparticles showed wormhole-like etching, more variations could contribute to higher roughness values

- RMS: 2.098 ± 1.50 nm
- CV plot shows broadening peaks and indicates roughness on the surface; presence of a double peak suggests different redox environments on the surface

- RMS: 3.112 ± 2.98 nm
- SEM imaging and AFM height analysis shows that roughness values are high because of the formation of silicon nanowires

Conclusions

Future Directions

- Modify roughness parameters to have more consistent, equally sized and spaced pits on the surface
- Experiment with lower concentrations of ferrocene and lower roughness values than flat samples to gain broad ranges and extreme values

Beyond the Scope

- Study on a different substrate; quantifying lateral interactions in self-assembled monolayers on silicon with varying topography and surface concentration
- Incorporate carbon dioxide reduction catalysts as a monolayer to understand how lateral interactions affect catalysis

Acknowledgements

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