MATERIALS AND METHODS

Sample Preparation:

The Au(111) single crystal and all components of the AFM 5500 fluid cell must be cleaned daily before experimentation. The cleaning procedure is as follows:

1. Fluid cell components (Teflon cell, o-ring, Pt₀.₈₀Ir₀.₂₀ counter electrode, and Pt reference electrode) and Au(111) crystal are submerged for 15 minutes in boiling nitric acid to enhance removal of any unwanted or adsorbed silver from prior experiments.
2. All components and crystal are rinsed in HPW and placed in piranha solution (3:1 concentrated H₂SO₄ to 30% H₂O₂) for an additional 15 minutes or overnight.
   a. If left overnight, counter electrode is rinsed once again with HPW after 15 minutes in piranha and then placed in 0.1M HClO₄ overnight to reach equilibrium with electrolyte solution
   b. Counter electrode is then rinsed in HPW and placed in 0.1M HClO₄ for 30 minutes to reach equilibrium with electrolyte solution
3. Cleaned components and crystal are then sonicated for 15 minutes in a FS-14 solid state/ultrasonic
4. Items are then rinsed 8 times in HPW and placed in beakers that have also undergone cleaning procedure filled with HPW for storage while piecing together fluid cell.
5. Au(111) crystal is hydrogen flame annealed at 1000K for 15 minutes.
6. Crystal is placed on conductive sample plate and the surface is quenched with HPW.
7. Fluid cell is put together around crystal.
8. HPW is removed from surface and replaced with 0.1M HClO₄ electrolyte solution.
9. Resistance between counter and reference electrode is tested and confirmed to be in MΩ range and conductivity across the surface is tested using multimeter.
10. Fully formed sample plate with fluid cell is then connected to AFM 5500 to begin experimentation.

Experimentation:

Monolayer Application and Imaging

All experiments are run in similar fashion and are performed using an Agilent branded AFM 5500 (now owned by Keysight Technologies).

1. Bare Au(111) surface is held at a positive potential of 0.10V vs Pt for 2 hours to ensure flattening of the intrinsic herringbone reconstruction.
2. CVs are taken to ensure a clean surface
3. Sample plate is removed from AFM 5500 and the electrolyte solution is replaced with saturated AgCl or AgBr in 0.1M HClO₄ in order to introduce Ag to the system.
4. Sample is reconnected to system and an application CV is taken by completing a single linear sweep from a more positive potential to experimentally determined underpotentials at a rate of 0.1 V/s
5. Sample is then held at final underpotential for 15 minutes to ensure maximum deposition onto surface.
6. Once monolayer is applied, imaging using STM scan head is performed.
   a. While imaging, sample potential is held at underpotential for the entirety of imaging to ensure any Ag monolayer imaged is from specific UPD event

Obtaining External CVs

All experiments are run on Bio-Logic SP-300 potentiostat vs Ag/AgCl electrode as reference and Pt mesh as counter.

1. CV of bare Au(111) crystal is obtained over full window from -0.4V to +0.8V to ensure innate oxidation and reduction peaks appear at appropriate potentials
2. Bare Au(111) crystal is held at a positive potential of 0.7V vs Ag/AgCl for 2 hours to ensure flattening of the intrinsic herringbone reconstruction.
3. CVs are taken within appropriate windows for region 1 or region 2 depending on experimentation.
4. Electrolyte solution is replaced with AgX in HClO₄ solution and a linear sweep is performed beginning at positive end of regional window and ending at deposition peak.
   a. Linear sweep is performed at 0.5 mV/s
5. A chronoamperometry experiment is then used to hold deposition potential across surface for 15 minutes
6. CV of region within window is taken at 0.1 V/s
   a. 3-5 cycles taken

Test for Thermal Stability

1. Remove sample with recently applied Ag monolayer from AFM 5500
2. Dismantle fluid cell and begin cleaning procedure for all components (excluding Au(111) crystal).
   a. This is to ensure any Ag residue is removed and cannot contaminate sample when testing for thermal stability
3. Flame anneal crystal for 15 minutes then reassemble sample plate with fluid cell
   a. Fill fluid cell with 0.1M HClO₄ to ensure no outside Ag source
4. Take CVs within UPD window to identify Ag UPD peak.
   a. If present then monolayer is thermally stable
   b. If absent then Ag was removed during annealing process and thermally instable

Materials

1. All electrochemistry and scanning was performed on an Agilent/Keysight PicoScan 5500 scanning probe microscope.
2. Tips used for imaging were Keysight Technologies N9802A, Apiezon wax coated Pt$_{0.8}$Ir$_{0.2}$ wire.
3. Data was acquired using the Agilent PicoTREC molecular recognition toolkit as well as an internal bipotentiostat.
4. PicoView software version 1.20 to collect the CV and STM data.
5. Single Au(111) crystal (Princeton Scientific Corp.) was used as the working electrode.
6. Counter electrode: Pt$_{0.8}$Ir$_{0.2}$wire.
8. Electrolyte consisted of ACS Optima Grade 0.1 M HClO$_4$.
9. Saturated AgCl solution made with ACS Optima Grade 0.1 M HClO$_4$ and Acros Organics 99.9999% Trace metal basis AgCl.
10. Saturated AgBr solution made with ACS Optima Grade 0.1 M HClO$_4$ and Alfa Aesar 99.998% metal basis AgBr.