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### Influence of 3-mercapto-1-propanesulfonic acid on the electrodeposition of Palladium at Au(111) electrode

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Self-assembled monolayers (SAMs) of organic sulfides on noble metal surface have been widely applied in different fields such as electroplating, sensors, microelectronic and light-emitting devices for its excellent physical and chemical nature (e.g. wetting, adhesion). In previous studies, researchers revealed that sulfur-containing organic molecules have a grain-refining effect on Cu deposition and the Cu growth behavior depends on SAMs, chloride ions. While the adsorption of SAMs was frequently reported as an additive to affect the growth behavior of copper deposition, sulfur-containing organic molecules like 3-mercapto-1-propanesulfonic acid (MPS) have never been used as surfactants for palladium deposition in the solution containing palladium ions.

Cyclic voltammograms (CV) were obtained with standard three-electrodes system, using platinum counter electrode and saturated calomel electrode as reference electrode. Au(111) electrodes was prepared by the Clavilier's method and electrodes were annealed in a hydrogen flame and quenched in ultrapure water with hydrogen before used. Then, Au(111) single crystal surface was immersed in  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{H}_2\text{SO}_4$  solution containing MPS and rinsed with ultrapure water for seconds. The EC-STM experiences were performed with NanoScope E scanning tunneling microscope and all the study was in the constant-current mode. The tips for EC-STM was made of Pt/Ir wires (Pt 80%) and produced by mechanical shear. Subsequently, tips were coated with polyethylene to decrease faradaic currents. Additionally, the potential was calibrated to saturated calomel electrode (SCE) in this paper. All solutions were prepared by ultrapure water (resistivity  $\geq 18 \text{ M}\Omega\cdot\text{cm}$ ) at room temperature.

The influence of 3-mercapto-1-propanesulfonic acid (MPS) on electrodeposition of palladium was established that MPS adsorbed strongly onto the electrode surface. Before the palladium deposition, MPS modified Au(111) electrode were measured in  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{H}_2\text{SO}_4$  by cyclic voltammograms. When stepping potential to  $-0.2 \text{ V}$ , Fig.1 showed that MPS molecules would appear to reductive desorption and oxidation desorption of MPS was found at  $0.6 \text{ V}$ . Therefore, stable range for MPS was between  $-0.1 \text{ V}$  and  $0.5 \text{ V}$ . Then, the MPS modified Au(111) electrodes was immersed in  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{H}_2\text{SO}_4$  containing  $\text{H}_2\text{PdCl}_4$  at the stable potential of MPS absorption and recorded by cyclic voltammetry (CV) and In-situ STM. In-situ STM (Fig.2) investigated the complex  $[\text{PdCl}_4]^{2-}$  prior to absorbed on MPS modified Au(111) single crystal surface. When potential shifted to  $0.515 \text{ V}$ , Pd complex reduced electrochemically to Pd onto the modified electrode. At  $0.32 \text{ V}$ , the electrochemical deposition of palladium forms via layer by layer and gradually covered with the whole MPS/Au(111) surface. However, the next layer start to nucleate before the former layer have been completed. After shifting potential to  $0.25 \text{ V}$ ,  $-0.1 \text{ V}$ , Pd islands were randomly scattered on the flat surface of electrodes and formed via 3D growth. Also the layers for Pd overdeposition became roughness and fraction for potential turning negative. Combination with the results of cyclic voltammetry, we established that MPS molecules decreased the amount of palladium electrodeposition and the potential for bulk palladium electrodeposition shifted to more negative and the potential of dissolution shifted to more positive. We should note that the behavior of electrochemical deposition for palladium had been changed. In the overpotential region, it should be observed 2-10 Pd overlayers on bare Au(111). After modifying MPS onto Au(111) electrode, the first underpotential Pd films still exit and the overlayers of Pd was replaced by roughness and friction appearance. Overall, this study established MPS molecules absorbed to Au(111) electrode inhibited palladium deposit and changed the Pd deposition mode onto Au(111).