

In Situ Scanning Tunneling Microscopy of Electrochemical Deposition of Mercury Films on Well-Ordered Iridium(111) Electrodes

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A mercury film supported by carbon and iridium substrates has found wide applications in electroanalyzing inorganic, organic, and biomolecules. These applications are made possible by the inherent merits of Hg as an electrode material, the higher surface-to-volume ratio and complete exhaustion of foreign metals. The Hg film electrode is shown to have good collection efficiency and sharp current transients. It is beneficial to use iridium as the support for Hg, because of the good wettability and its low solubility in Hg. In contrast, Hg can mix with a gold or platinum substrate at room temperature, thereby producing amalgam phases, which degrade the precision of electroanalytical measurements.

With the advance of modern technology, sophisticated spectroscopies, such as second-harmonic generation and X-ray scattering have replaced the traditional thermodynamic approach relying on measuring the surface tension of dropping mercury electrodes. Scanning probes of the scanning tunneling microscope (STM) and atomic force microscope have been applied in electrolyte to examine the electrodeposition of Hg onto polycrystalline Au, and smooth and columnar Pt electrodes. Hg is found to alloy readily with Au and potentially this is possible with rough Pt electrodes at room temperature. Meanwhile, underpotential deposition (upd) of Hg at single crystal Au electrodes has been examined by electrochemical means and scanning probes. Hg atoms are adsorbed in highly ordered mixed adlayers with sulfate or chloride. Bulk Hg deposition unanimously yields 3D islands on Au(111) and produces alloys simultaneously. Furthermore, the adsorption of Hg at solid substrates is relevant to the analysis of Hg as a contaminant in gaseous samples. STM has been used to examine the kinetics of Hg adsorption on Au and Ag substrates from the gas phase, indicating the formation of surface alloys mainly at step defects. Atomic resolution STM imaging also reveals the structure of a HgCl<sub>2</sub> monolayer on Au(111).

We have employed linear sweep voltammetry (LSV) and in situ scanning tunneling microscopy (STM) to examine the electrodeposition of Hg at a well-ordered Ir(111) electrode in aqueous 0.1 M HClO<sub>4</sub> containing dilute Hg(ClO<sub>4</sub>)<sub>2</sub>. The results of LSV revealed multiple peaks, presumably due to underpotential deposition and diffusion-limited bulk deposition. In situ STM unveiled the details of bulk Hg deposition at bare and iodine-modified Ir(111). The compositions of the Ir(111) surface could dominate the morphology of the Hg film. An iodine adlayer rendered layer-by-layer deposition of Hg till the sixth layer when 3D island growth prevailed. High-quality STM atomic resolution identified a well-ordered iodine overlayer residing on top of the Hg film, strongly

suggesting that the Hg film was crystalline. At a bare Ir(111), Hg deposition was also layer-by-layer but only to a thickness of three layers. Without the iodine adlayer, the Hg film was, however, seriously pitted and it was not possible to achieve atomic resolution.

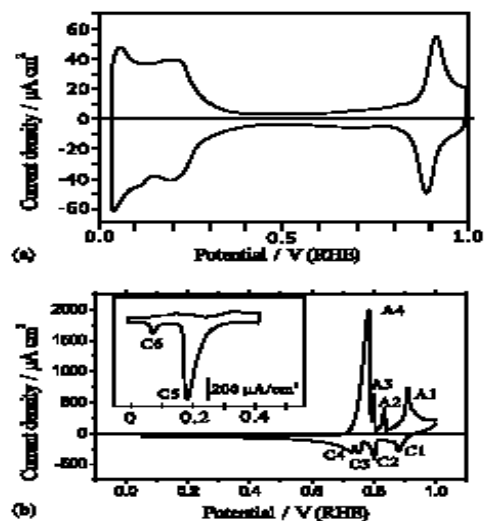


Fig. 1. Cyclic voltammograms at 50 mV/s of an ordered Ir(111) electrode in 0.1 M HClO<sub>4</sub> (a) in 0.1 M HClO<sub>4</sub> 1 mM Hg(ClO<sub>4</sub>)<sub>2</sub> (b) The inset in (b) highlights the profile between 0 and 0.4 V, obtained in a solution of 0.1 M HClO<sub>4</sub> containing 0.1 mM KI and 1 mM Hg(ClO<sub>4</sub>)<sub>2</sub>.

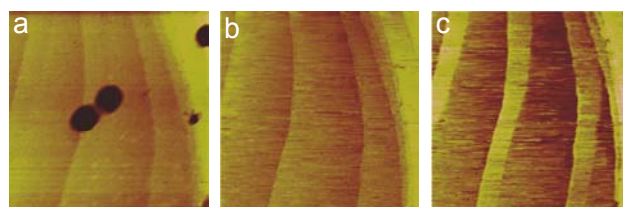


Fig. 2. Time-sequenced in situ STM images revealing the deposition of Hg on an iodine-modified Ir(111). The dark regions were pits produced in the annealing and dosing of iodine vapor.

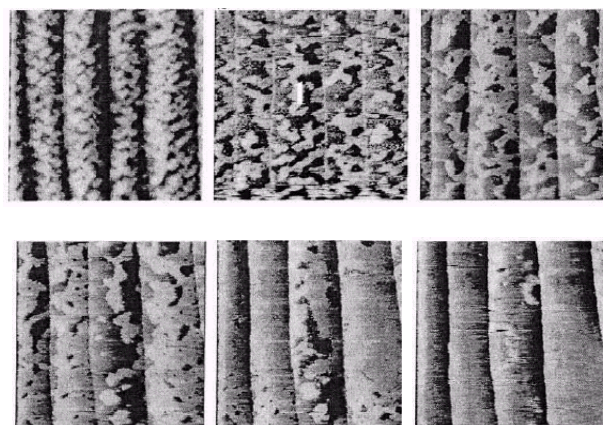


Fig. 3. Time-dependent in situ STM images of electrodeposition of a Hg layer on Ir(111) modified with a monolayer of iodine adatoms. This sequence of STM images span 2:28 min.

Reference:

Y. S. Yang et al *J. Electroanal. Chem.* **2003**, 556, 53.