Kinetics of Pt Monolayer on Au Surface During SLRR

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Kinetics of platinum monolayer formation via the redox replacement of underpotentially deposited copper on a Au(111) electrode surface by a platinum tetrachloride complex ($PtCl_4^{2-}$) was studied by CV, XPS, QCM, and STM. The Pt $4f_{7/2}$ peak intensities of XPS and voltammetric responses of H adsorption/desorption increased as the incubation time increased in $PtCl_4^{2-}$ solutions. The resonance frequency of the Cu/Au QCM in H_2SO_4 solution was observed to quickly decrease within 1 min when it contacted with $PtCl_4^{2-}$ solutions, and then it remained unchanged for hours. EDS data showed that Cu was not found at high $PtCl_4^{2-}$ solutions. Ex situ STM images revealed a largely uncovered Au(111) surface with mountain-like Pt nanoparticles at a replacement time of 10 min, and mostly covered Au(111) one with plain-like Pt nanoparticles of 4 h. The average size of Pt particles decreased approximately logarithmically as a function of time, whereas the number of Pt particles increased. Thus, after replacement, Pt atoms were dynamic in hours, resulting in a flattened Pt monolayer. A mechanism that includes reverse Ostwald ripening is provided to rationalize the observations.