

Lead Underpotential Deposition on Ru Sub-Monolayer Modified Au(111) Surface

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The underpotential deposition (UPD) is the process with fundamental and practical importance. During 1960's and 1970's the extensive studies of many UPD systems were performed on single crystal and polycrystalline electrodes¹. Development of scanning probe methods (STM and AFM), and X-ray scattering techniques has renewed the interest for *in situ* UPD studies. In 1980's and 1990's many UPD systems on single crystal substrates were re-examined in great detail². However, a few works has been done studding the UPD on bi-metallic surfaces, alloy surfaces³ or surfaces modified with submonolayer of foreign metals⁴.

Our talk reports study of Pb UPD on Ru submonolayer modified Au(111). The controlled amount of Ru on Au(111) was deposited using spontaneous deposition. The example of the cyclic voltammetry and insitu STM results studying the Pb UPD process on Ru submonolayer modified Au(111) are shown in Fig. 1A. The potential has been gradually changed towards the region where Pb UPD on Au(111) and Ru(0001) occurs and high resolution/quality STM images were recorded, Fig 1A. These images were analyzed using sophisticated image processing algorithm where the cluster density, Au(111) coverage, and mean cluster size were analyzed as a function of the electrode potential, Figure 1B. The STM results show that the initial stage of the UPD process starts by decoration of the 2D Ru nanoclusters. The gradual increase in the area of the Ru nanoclusters occurs in the potential range of the first UPD peak, ΔE between -325 mV and 225 mV vs. Pb²⁺/Pb ref. electrode. Further UPD process continues with Pb gradual attachment to the portion of the outer Pb layer-decorating the Ru nanoclusters, Figure 1B. The statistical analysis shows that the initial area/size of Ru clusters increases by 400% during potential limits of the first UPD peak. At the same time, neither significant increase in the cluster density on the surface nor the nucleation of Pb clusters on top of the existing Ru nanoclusters is observed. This means that Pb deposited at the perimeter of the Ru nanoclusters becomes their dominant portion at $\Delta E=225$ mV. The main findings, similarities and differences between UPD on single crystal Au(111), Ru(0001) and Ru -modified Au(111) systems will be presented and discussed.

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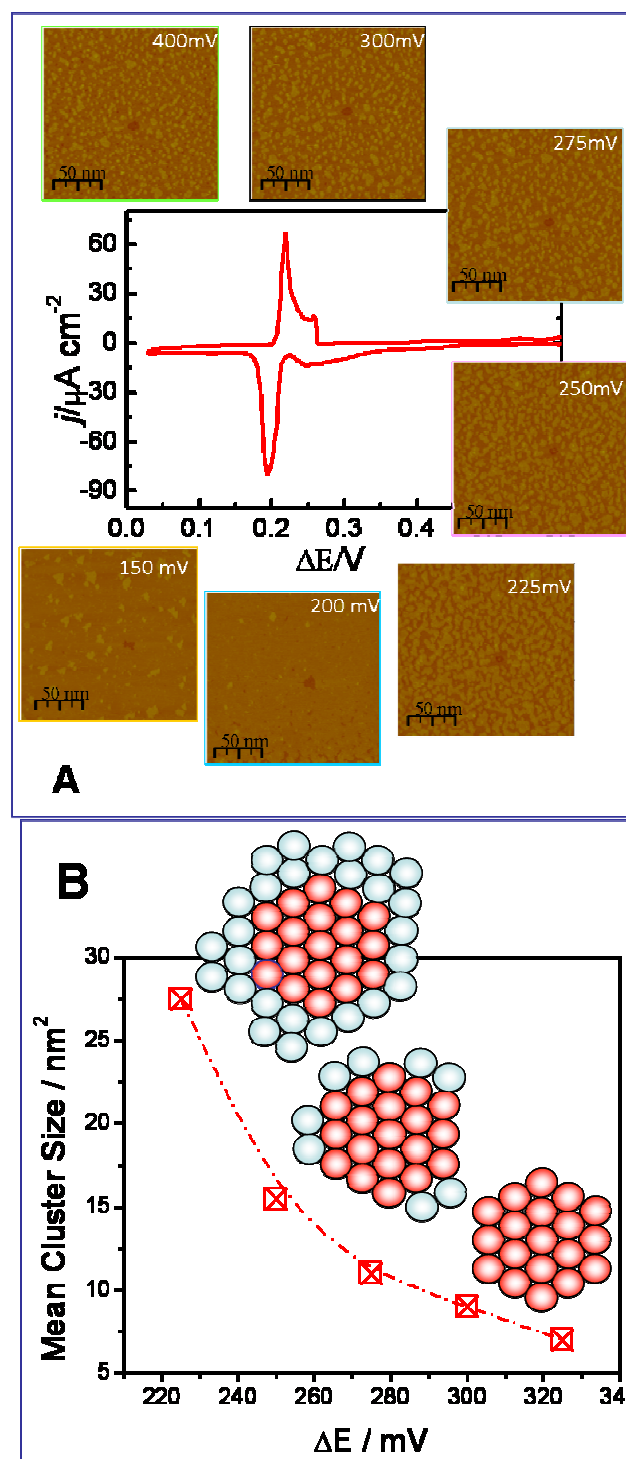


Figure 1. (A) Cyclic voltammetry results for Pb UPD on Ru modified Au(111), scan rate at 20 mV/s. The STM images of Ru modified Au(111) are shown with corresponding potentials (B) The statistical analysis of STM data showing the mean size of clusters as a function of underpotential. The cartoon describes the initial stage of Pb UPD on Ru nanoclusters.

¹ S. Trasatti, *J. Electroanal. Chem.* 33, 351 (1971),

² E. Budevski, G. Staikov and W. J. Lorenz in *Electrochemical Phase Formation and Growth*, ed. R.C. Alkire et al. VCH, Berlin (1996), see Ref. herein.

³ C. McCall, N. Dimitrov, and K. Sieradzki, *Journal of the Electrochemical Society*, **148**, E290, (2001).

⁴ Q. Yuan, A. Tripathi, M. Slavkovic, and S.R. Brankovic, *Z. Phys. Chem.*, 226, 965 (2012).

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