Lead Underpotential Deposition on Pt-submonolayer Modified Au(111)

By Qiuyi Yuan¹, Ashish Tripathi¹, Milan Slavkovic², and Stanko R. Brankovic¹,³,*

¹ Electrical and Computer Engineering Department, University of Houston, Houston Texas, 77204, USA
² Biomedical Engineering Department, University of Houston, Houston Texas, 77204, USA
³ Chemical and Biomolecular Engineering Department, University of Houston, Houston Texas, 77204, USA

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Lead underpotential deposition on Au(111) surface modified with submonolayer of Pt is studied using cyclic voltammetry and in situ scanning tunneling microscopy methods. The two-dimensional Pt submonolayers (nanoclusters) on Au(111) were obtained by spontaneous Pt deposition on Au(111) from $10^{-3} \text{M} \{\text{PtCl}_6\}^2^+ + 0.1 \text{M HClO}_4$ solution. The in situ scanning tunneling microscopy data were analyzed using statistical image processing algorithm which enabled quantification of the morphology change on Pt-modified Au(111) surface as a function of applied underpotential. The results suggest that Pb underpotential deposition starts on Au steps and other surface defects, similar to Pb underpotential deposition on Au(111). The further process proceeds by Pb monolayer nucleation and growth on Au terraces into a complete layer. In parallel, the Pb monolayer starts to nucleate on top of the Pt nanoclusters. The final stage of the Pb underpotential deposition is formation of the compact Pb nanoclusters/layer on top of the pre-existing Pt nanoclusters. The scanning tunneling microscopy data suggests that morphology of underpotentially deposited Pb monolayer on Pt-modified Au(111) is similar to the starting surface in terms of the areal density of nanoclusters, their size and shape. The morphological changes of the Pt modified Au(111) surface during Pb underpotential deposition are correlated with cyclic voltammetry results.

1. Introduction

The underpotential deposition (UPD) phenomenon has been extensively studied over the years. Rogers et al. performed one of the first studies of UPD in the late 1940’s investigating the deposition of radioactive Ag on polycrystalline Au and Pt [1]. During the 1960’s and 1970’s the extensive electrochemical studies of many UPD systems were performed on single crystal and polycrystalline electrodes [2,3]. Development of scanning probe microscopy and X-ray scattering techniques capable of in situ investigation of surface structures with atomic resolution have renewed the interest for UPD studies.

* Corresponding author (E-mail: stanko.brankovic@mail.uh.edu).
In 1980's and 1990's many UPD systems on single crystal substrates were re-examined in great detail providing more insight and information about UPD phenomenon, its description, and diversity [4,5].

The UPD represents potential dependent adsorption process with great sensitivity and selectivity towards nature of the metal surface, its structure and termination [2,4]. As such, the UPD has been used as decoration technique for surface characterization in corrosion studies [6], measurements of surface area [7] or characterization of thin film quality and surface roughness [8,9]. The UPD precedes the bulk deposition in many heteroepitaxial systems which enables applications of this phenomenon in different electrochemical deposition protocols [9–13]. The UPD monolayers are often used for surface decoration of catalytically active metals providing a route for enhancement of catalyst activity and selectivity towards certain reactions [14]. In recent years, the new protocol for fuel cell catalyst synthesis was developed [8,15,16] where UPD plays a crucial step. In this approach, catalyst is deposited via surface limited red-ox replacement (SLRR) of UPD monolayers which has led to implementation of the active monolayer concept where the ultimate specific activity and minimum loading of precious metals is achieved [17,18]. Further development of UPD-based catalyst monolayer synthesis protocols are limited by our lack of the detailed knowledge about UPD process where the substrate is the metal surface modified with submonolayer of different noble metal. More information in this area will provide an avenue for achieving a precise control of the catalyst monolayer morphology, coverage and composition. Obtaining the details of the UPD process on metal surfaces modified by different noble metal submonolayer will undoubtedly help sophistication of the catalyst synthesis protocols via SLRR with possibility to control and design the catalysts at true atomic scale.

This paper reports study of the Pb UPD on Au(111) modified by Pt submonolayer (Pt$_{SML}$Au(111) in further text) using cyclic voltammetry (CV) and in situ scanning tunneling microscopy (STM) methods. This system/substrate has a great relevance for the field of electrocatalysis where Pt monolayers have been explored as catalysts for fuel cell application. The study of Pb UPD on Pt$_{SML}$Au(111) provides a stepping stone for further exploration of the catalyst design via SLRR towards formation of bi-metallic catalyst monolayers or Pt monolayers with larger coverage using repetitive SLRR.

The two-dimensional Pt submonolayers were deposited by spontaneous Pt deposition on freshly annealed Au(111) surface [19,20]. The in situ STM data were quantified using statistical image processing algorithm, enabling the quantitative estimate of the surface coverage and nanoclusters' shape and areal density as a function of applied underpotential [20,21]. The morphology changes of Pt$_{SML}$Au(111) surface during Pb UPD are discussed and correlated with cyclic voltammetry results.

2. Experimental

The working electrode was Au(111) single crystal (Monocrystals Company) prepared using several steps including mechanical polishing, electropolishing and hydrogen flame annealing [10,11]. The typical outlook of freshly prepared and annealed Au(111) surface is presented in Fig. 1. The Au surface is characterized with $\geq$ 0.5 micron
Fig. 1. The representative 500 nm × 500 nm STM image of the Au(111) surface after mechanical polishing, electropolishing and H₂ flame annealing.

large terraces separated with steps and step bunches. All solutions used in our experiments were made with ultra high purity chemicals (99.999%, Alfa Easer, Merck) and 18.2 MΩ-cm ultrapure water (Millipore Direct Q-UV with Barnstead A1007 pre-distillation unit). The PtSML/Au(111) surface was obtained using spontaneous deposition process which involved immersion of freshly prepared/annealed Au(111) into 10⁻³ M{PtCl₆}²⁻ + 0.1 M HClO₄ solution for 30 s and subsequent rinse with ultrapure water [19]. Such prepared PtSML/Au(111) surface has shown Pt-like behavior during potential cycling in 0.05 M H₂SO₄ characterized by modest appearance of hydrogen UPD/stripping and Pt-OH formation/reduction peaks. The solution used to study Pb UPD on PtSML/Au(111) was 10⁻² M Pb²⁺ + 0.1 M HClO₄. All solutions were deaerated with ultra pure argon for 2 h before experiments. All potentials in this study are quoted vs. saturated calomel electrode (SCE) or they are discussed and presented as the value of underpotential.

All electrochemical experiments and in situ STM studies were performed in nitrogen-purged glove box to minimize the effect of oxygen on STM imaging and possible oxidation of Pt deposit during crystal transfer from one solution to another. The in situ STM images were recorded using the Nanoscope V controller with multimode scanner unit (Veeco instruments). For this purpose, the custom electrochemical cell was built to support our in situ STM experiments. The cell was made out of Teflon hav-
ing the volume of 3 cm$^3$ and possibility of electrolyte addition during STM imaging. The reference electrode in STM studies was 1 mm diameter Pb wire, (Pb$^{2+}$/Pb) and the counter electrode was 0.5 mm diameter Pt wire. The Au(111) single crystal disk with diameter of 10 mm served as working electrode. The in situ STM images of the Pb UPD process on Au(111) and on Pt$_{SML}$/Au(111) were analyzed using our custom made digital image processing (DIP) algorithm [22]. For this purpose, a threshold value has been determined to segment each image into a binary image using an autonomous global thresholding method [23]. The image segmentation was used for differentiation and identification of each nanocluster on the surface. To minimize the effect of drift, from each recorded STM image (225 $\times$ 225 nm), the 75 $\times$ 75 nm portions of the flat terrace with identical spatial position were identified and processed using DIP algorithm. This analysis provided an objective information about the number of Pt and Pb nanoclusters on Au(111) terraces, the mean/representative size of the nanoclusters, their coverage and height [21,24]. The error bars for STM-based results represents the $\pm$ standard deviation of the data obtained from the analysis of each image recorded at particular underpotential.

3. Results and Discussion

3.1 Pb UPD on Au(111)

The Pb UPD on Au(111) in perchloric acid electrolyte has been studied in great detail by many authors using variety of electrochemical and in situ characterization techniques [4,5]. This system has direct phenomenological relevance to our study of Pb UPD on Pt$_{SML}$/Au(111) surface. Because of that, our in situ STM and voltammetry data for Pb UPD on Au(111) are reviewed first as a prelude to the main discussion regarding the Pb UPD on Pt$_{SML}$/Au(111).

In Fig. 2, the CV of the Pb UPD on Au(111) is presented. The shape of voltammogram and characteristic features are in very good agreement with previously published data [25–27]. The main Pb UPD peak is very sharp and occurs at approximately $+0.18$ V underpotential. This peak is preceded by several smaller and broader cathodic peaks, which occur at higher underpotentials (0.25 $\times$ 0.240 V). Results from literature regarding the onset underpotential for Pb UPD on Au(111) in perchloric acid electrolyte vary, depending on the quality of the Au(111) surface and preparation routine. The general agreement is that UPD process starts with adsorption of Pb or Pb-OH species on the surface defects such as steps and dislocations [5]. The starting Au(111) surface is shown in Fig. 3a at $\Delta E = 0.600$ V. At this potential no Pb UPD layer is present on Au surface. Changing potential to $\Delta E = 0.300$ V a significant change of the contrast in STM images is observed at steps which is associated with the Pb step decoration and the onset of Pb UPD on Au(111) (Figs. 3a vs. 3b, arrows). Thus, in agreement with previous reports [4,5,28], the broad cathodic peak at $\approx 0.375$ V (Fig. 2) is associated to the initial decoration of the Au(111) surface defects by Pb adatoms or Pb-OH adsorbed species. Further change of underpotential in cathodic direction to 0.275 V induces appearance of the first Pb UPD nuclei at the Au(111) terraces, Fig. 3c. The nucleation process advances further as the underpotential is changed to 0.250 V. At this potential, the significant portion of the Au(111) terrace is covered with Pb UPD nu-
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Fig. 2. The cyclic voltammetry of Pb UPD on Au(111) surface. Solution: $10^{-2} \text{ M Pb}^{2+} + 0.1 \text{ M HClO}_4$, sweep rate 0.02 V s$^{-1}$. The underpotential, at which each STM image is recorded in Fig. 3, is indicated in the graph.

Fig. 3. The 175 nm $\times$ 175 nm $\textit{in situ}$ STM images of Pb UPD on Au(111) surface. The underpotential of the Au(111) surface is indicated in the lower left corner of each image. Solution: $10^{-2} \text{ M Pb}^{2+} + 0.1 \text{ M HClO}_4$.

clei, Fig. 3d. Decreasing the underpotential to $\Delta E = 0.225 \text{ V}$ the Pb nuclei begin to coalesce and an incomplete but continuous Pb UPD layer becomes apparent, Fig. 3e. According to our STM and CV data, the broad shoulder and cathodic peak at $\approx 0.235 \text{ V}$ shown in the CV, Fig. 2, are associated with nucleation and growth of Pb UPD layer on Au(111) terraces [5]. Reducing the underpotential further to 0.200 V and entering the potential range within the main Pb UPD peak, the morphology of the surface indicates completion of Pb UPD layer on Au(111) surface, Fig. 3f. Further reduction of
Fig. 4. The cyclic voltammetry of Pb UPD on PtSML/Au(111) and Pt(111) surfaces. Solution: $10^{-2}$ M Pb$^{2+}$ + 0.1 M HClO$_4$, sweep rate 0.02 V s$^{-1}$. The underpotentials at which each STM image is recorded in Fig. 5, is indicated in the graph.

the underpotential to 0.15 V, just outside of the main UPD peak, does not produce any morphological change on the surface (Fig. 3g). This indicates that the most of the current/charge associated with the main Pb UPD peak is related to densification of the UPD layer which initially nucleates and grows as low-density phase [4]. The STM images in Figs. 3f and 3g are almost 1 : 1 replica of the starting Au(111) surface, Fig. 3a. At 0.100 V underpotential, a fully dense Pb UPD phase forms with incommensurate hexagonal structure and $\approx 7\%$ smaller interatomic distance then the bulk Pb, [26]. The atomic resolution STM image of the Pb UPD layer on Au(111) at this potential is shown in Fig. 3h. The moiré pattern in the image indicates compression in the Pb UPD layer [4,26]. The data presented in Figs. 2 and 3 are in agreement with previous reports [4,5,25–28].

3.2 Pb UPD on PtSML/Au(111)

In Fig. 4, the CV for Pb UPD on PtSML/Au(111) (red) and Pt(111) surface (blue) are presented. The main Pb UPD peak on Pt(111) occurs approximately at $\Delta E \approx 0.750$ V. It is preceded by two smaller and broader peaks occurring at higher underpotentials related to Pt-OH reduction and probable Pb-OH adsorption as a prelude to the Pb UPD process [29]. The smaller deposition peaks occurring at lower underpotential then the main Pb UPD peak are associated with gradual densification of the Pb UPD layer and formation of different phases. The $\sqrt{3} \times 3$ structure has been identified as the densest one forming at 0.300 V underpotential [29].

The PtSML/Au(111) surface used in our study is characterized with population of 2D Pt nanoclusters having the mean size, $S_{Pt,mean} \approx 16 \pm 4 \text{ nm}^2$ and Pt coverage of the
Fig. 5. The 225 nm × 225 nm in situ STM images of Pb UPD on PtSML/Au(111) surface. The underpotential of the surface is indicated in the lower left corner of each image. Solution: $10^{-2}$ M Pb$^{2+}$ + 0.1 M HClO$_4$.

Au(111) terrace of 12 ± 1%, (Figs. 5a, 6a and 7). The areal density of the Pt nano-clusters on Au(111) is $n_{Pt} = 0.14 \times 10^{13}$ cm$^{-2}$ which means that the average distance between the centers of neighboring nanoclusters is $< l_{Pt} > \approx 8.5$ nm ($\sqrt{n_{Pt}}$), Fig. 7a. Our analysis of the area/perimeter ratio for deposited Pt nanoclusters shows that great majority of them have compact shape. The CV for Pb UPD on such PtSML/Au(111) surface, Fig. 4, indicates that the main UPD peak occurs at $\Delta E \approx 0.215$ V. This is very close to the value of underpotential where the main Pb UPD peak is observed on Au(111), Fig. 2. The broad cathodic peak at $\Delta E = 0.440$ V and smaller one at $\Delta E = 0.260$ V preceding the main peak occur around the same potentials as their counterparts in Pb UPD on Au(111) system. However, all cathodic peaks in CV for Pb UPD on PtSML/Au(111) surface are slightly shifted towards higher underpotentials than the ones observed for Au(111) surface. In general, the main voltammetry features of Pb UPD on PtSML/Au(111) are similar to Pb UPD on Au(111). This result is somewhat expected knowing that only 12% of the Au(111) surface is covered with 2D Pt nanoclusters. However, it is surprising that no cathodic peak is observed in CV data in the underpotential range where the main Pb UPD peak occurs on Pt(111).

The in situ STM images following the Pb UPD on PtSML/Au(111) surface are presented in Fig. 5a–k. The results obtained from processing these STM images are shown...
in Figs. 6 and 7. The schematics explaining the relationship between the results in the graphs and morphology of the surface (1\textsuperscript{st} layer vs. 2\textsuperscript{nd} layer) is presented in Fig. 6b.

The starting Pt\textsubscript{sML}/Au(111) surface is held at 0.800 V underpotential. In agreement with our CV data, our STM measurements indicate that no Pb is present on top of Pt nanoclusters, and on top of Au(111) surface. The average height of Pt nanoclusters is 0.33 nm, which is slightly higher then for a monolayer high Pt nanocluster. This might be indication that adsorbed OH layer is present on top of the Pt nanoclusters at this underpotential. The small size and high curvature of 2D Pt nanoclusters promote their reactivity and it is reasonable to expect presence of the stable Pt-OH layer on top of Pt nanoclusters even at potentials more negative than the Pt-OH reduction potential for bulk Pt(111) [30]. Reducing the underpotential further to 0.600 V no morphological change is observed on Pt\textsubscript{sML}/Au(111), Fig. 5b. There is no indication that Pt nanoclus-
ters’ height or size has changed appreciably, (Figs. 6 and 7). Considering that CV data show that the main Pb UPD peak on Pt(111) [29,31] occurs at 0.750 V, Fig. 4, it is a bit unexpected that there is no decoration of Pt nanoclusters with Pb adatoms observed at this STM image/potential. However, the lack of Pb layer on top of Pt nanoclusters is in agreement with our CV data that show lack of any cathodic peak in this potential range. We attribute this apparent passivity of Pt nanoclusters to the presence of Pt-OH layer [29,30] but we cannot rule out the ligand effect of Au substrate in modifying the electro sorption properties of Pt nanodeposit [14].

Further reduction of underpotential to 0.550 V and 0.500 V does not cause any visible changes in morphology of PtSML/Au(111) surface, Fig. 5c,d. The analysis of the STM images does not imply that there is any appreciable change of the nanoclusters’ areal density, coverage or size in the 1st layer. The decrease in underpotential further to 0.450 V and 0.400 V does not produce any obvious changes on the electrode surface, Fig. 5e,f. However, from the analysis of the STM images using DIP algorithm, the onset of morphological changes is evident, Figs. 6 and 7.

The fluctuation/changes in the 1st layer coverage starts with slight decrease (0.450 V) followed by an increase (0.400 V) in nanocluster areal density. These changes are mirrored with an increase (0.450 V) and then decrease (0.400 V) of the mean size of nanocluster population in the 1st layer. In this potential range, the CV data show a broad cathodic peak centered at 0.440 V underpotential. In electrochemical sense, the cathodic peak/current indicates the reduction process, and in our case, this could be associated with reduction of the Pt-OH phase to clean Pt nanocluster surface, or to reduction of Pb2+ ions to Pb adatoms. According to the CV data for Pb UPD on Au(111), Fig. 2, decoration of Au surface defects by Pb adatoms starts for any ΔE < 0.500 V, and we should expect the same to occur at defects sites present on the portion of the Au surface which is free from Pt nanoclusters. However, the charge associated with the cathodic peak centered at 0.440 V for PtSML/Au(111) surface is larger then the corresponding peak for clean Au(111). This means that additional reduction process takes place in parallel to the onset of Pb UPD process. In addition, the height of Pt nanoclusters at these potentials has decreased to expected value for Pt monolayer (0.270 nm). Therefore, we conclude that cathodic peak at 0.440 V and corresponding changes observed in STM images (Figs. 6a and 7) are related to simultaneous reduction of the Pt-OH phase and decoration of the defects on Au surface by Pb UPD adatoms.

The decrease of underpotential below 0.400 V produces significant changes in morphology of PtSML/Au(111) surface. At 0.350 V, the increase in number of 2D nanoclusters is clearly visible; Fig. 5g. This is quantified by a 30% increase in the areal density of the nanoclusters in 1st layer (from 0.16 × 10^13 cm^-2 to 0.21 × 10^13 cm^-2) and simultaneous decrease in mean size of the nanocluster population, Fig. 7b. These morphological changes are indicative of the nucleation event which means that this potential represent the onset of Pb UPD on free Au(111) terrace. At ΔE = 0.300 V and 0.250 V the growth of Pb UPD phase on Au surface continues which is quantified with further 20% and 40% increase of the 1st layer coverage and 5 and 500 times increase of the mean size of the nanoclusters population in the 1st layer (Figs. 5h, 5i, 6a and 7a). The dramatic decrease in areal density of nanoclusters in the 1st layer suggests that growth stage takes place, i.e. the Pb UPD nanoclusters grow and merge into a full monolayer on Au(111) terrace. This is obvious in Fig. 5i.
Fig. 8. Schematics of the Pb UPD on PtSML/Au(111). The encircled entities (S1) and (S2) represent different scenarios during UPD process. (S1) nucleation of more than one Pb UPD nanoclusters on top of Pt nanocluster, and (S2) merging of two Pb nanoclusters into a bigger one on top of the two Pt nanoclusters.

At $\Delta E = 0.300 \text{ V}$ (Fig. 5h), the nucleation of the 2$^{\text{nd}}$ layer is observed. The nanoclusters areal density in the 2$^{\text{nd}}$ layer is $\approx 7$ times larger than the initial density of Pt nanoclusters on Au(111). This indicates that several Pb nuclei form per one Pt nanocluster. The inset in Fig. 5h shows 6 Pb UPD nuclei formed on top of the pre-existing 20 nm$^2$ large Pt nanocluster. The mean size of the observed Pb nanoclusters nucleating in the 2$^{\text{nd}}$ layer is $\approx 2$ nm$^2$. Based on the analysis of STM images in this potential range and CV data for Pb UPD on PtSML/Au(111) we conclude that cathodic peak centered at 0.260 V underpotential is associated mainly with nucleation and growth of Pb UPD monolayer on Pt-free Au surface with simultaneous nucleation of Pb UPD monolayer on top of the Pt nanoclusters and their lateral decoration with Pb UPD adatoms in the 1$^{\text{st}}$ layer.

The decrease of underpotential to 0.200 V (Fig. 5j) and 0.150 V (Fig. 5k) results in morphological changes on PtSML/Au(111) which are related to completion of the Pb UPD process in both layers; On Pt-free Au surface (1$^{\text{st}}$ layer) and on top of pre-existing Pt nanoclusters (2$^{\text{nd}}$ layer). The main UPD peak in CV data for PtSML/Au(111) surface is associated with this stage, Fig. 4. The coverage of the 1$^{\text{st}}$ layer increases to 100% while the nanocluster density drops to 1 indicating morphology of a full Pb UPD layer filling the space on Au terraces in-between the pre-existing Pt nanoclusters, Figs. 6a and 7a. At the same time, the areal density of the nanoclusters in the 2$^{\text{nd}}$ layer drops about 10 times (from $0.8 \times 10^{13}$ cm$^{-2}$ to $0.08 \times 10^{13}$ cm$^{-2}$) which is the value $\approx 40\%$ lower than the initial areal density of Pt nanoclusters on the starting PtSML/Au(111) surface ($0.14 \times 10^{13}$ cm$^{-2}$). The mean size of the nanocluster population in the 2$^{\text{nd}}$ layer increases significantly ($S_{\text{Pb-mean}} = 30 \pm 7$ nm$^2$, Fig. 5k) and represents $\approx 2$ times larger mean size than what has been observed for initial population of Pt nanoclusters on PtSML/Au(111) surface (Fig. 5a, $S_{\text{Pt-mean}} = 16 \pm 4$ nm$^2$). The coverage of the Pb in the 2$^{\text{nd}}$ layer is 18%, Fig. 5k, which is $\approx 50\%$ larger than what is observed...
for the initial coverage of the Pt submonolayer (Fig. 5a, 12%). The smaller number but larger size and coverage of Pb nanoclusters in the 2nd layer suggest that Pb UPD on top of the pre-existing Pt nanoclusters does not replicate the exact morphology of the initial PtSML/Au(111), but a similar one. The following discussion will elaborate a few important points to explain the observed morphological difference between starting PtSML/Au(111) (Fig. 5a) and Pb UPD monolayer covered PtSML/Au(111) surface (Fig. 5k).

The increase of comparative area/coverage of Pb UPD layer on top of underlying Pt submonolayer is expected due to a size difference between Pt and Pb atoms (0.27 nm vs. 0.36 nm). The relaxed Pb nanocluster comprising the 2nd layer with the same number of atoms as the underlying Pt nanocluster in the 1st layer should have about 70% larger area. However, the full Pb UPD monolayer on Pt(111) has $\sqrt{3} \times 3$ lattice with 0.66 packing density [29]. If the same structure is assumed for Pb nanocluster on top of pre-existing Pt nanocluster, the total area/coverage of the Pb in 2nd layer ($\Delta E = 0.150$ V) should be $\approx 46\%$ larger ($46\% = 70\% \times 0.66$). Our measurements for the total Pb UPD coverage in the 2nd layer (Figs. 5k and 6a) show 50% larger coverage than pre-existing Pt submonolayer (1st layer, Figs. 5a and 6a). Evidently, the measured difference is very close to what we have calculated, (50% vs. 46%). Such good agreement suggests that the structure of the Pb UPD clusters formed on top of pre-existing Pt nanoclusters is most likely the same or close to the one observed for the full Pb UPD monolayer on Pt(111) [29].

The mean size of the Pb UPD nanocluster population measured at $\Delta E = 0.150$ V (2nd layer) is $\approx 30$ nm$^2$ which is 100% bigger than the mean size of the Pt nanocluster population in the starting PtSML/Au(111), (16 nm$^2$, $\Delta E = 0.800$ V). The number of Pb nanoclusters in 2nd layer is 40% smaller than the number of Pt nanoclusters in the starting PtSML/Au(111). Obviously, this morphological difference between Pb UPD layer on top of the starting Pt submonolayer cannot be explained using only arguments about physical size difference between Pt and Pb atoms and packing density of the Pb UPD on Pt(111). It seems that the arrangement of the Pb UPD nanoclusters in the 2nd layer is different than what we expect form the spatial position and distribution of underlying Pt nanoclusters, Figs. 5a vs. 5k. At $\Delta E = 0.150$ V where the STM image with complete Pb UPD on PtSML/Au(111) is recorded the formation of stable Pb nanoclusters on top of the PbUPD/Au(111) is unlikely process and it cannot be considered as explanation for morphological difference between PbUPD/PtSML/Au(111) and PtSML/Au(111) surfaces. However, the merging of two or more Pb nanoclusters into a bigger one sitting on top of two or more smaller Pt nanoclusters is possible scenario that can explain our results. To elaborate further, we point out that morphology of the initial PtSML/Au(111), Fig. 5a, is characterized with Pt nanocluster population having very small nearest neighbor center to center spacing, $\langle l_{\text{Pt}} \rangle = 8.5$ nm. The most of the Pt nanoclusters are compact in size and it is reasonable to assume their shape as disk-like with the equivalent diameter as representative linear dimension ($d_{\text{Pt-mean}} = \frac{4}{\pi} S_{\text{Pt-mean}} = 4.5$ nm). According to previous arguments if follows that each Pb UPD cluster on top of the Pt one has $\approx 50\%$ larger area and $\approx 23\%$ larger diameter ($d_{\text{Pb/Pt}} \approx 1.23 \times d_{\text{Pt}}$). It is reasonable to expect that within the Pt nanocluster population many of them have smaller center to center nearest neighbor distance than value calculated from the initial Pt nanoclusters areal density...
\( (\sqrt{n_{\text{Pt}}}, \Delta E = 0.150 \text{ V}) \). Therefore, the local variation in the areal density and nearest neighbor distance within the Pt nanocluster population can lead to scenario where the corresponding Pb UPD clusters forming on top of Pt are merged due to their bigger size. From geometrical point of view this scenario is possible whenever the center to center distance between neighboring Pt nanoclusters, \( (l_{\text{Pt}} = \sqrt{n_{\text{Pt}}} \) ), is less than 1.23 times the sum of the neighboring Pt nanoclusters’ diameters \( (l_{\text{Pt}} < 1.23 \times \sum d_{\text{Pt,i}}) \). If this condition is fulfilled, then instead of formation of 2 or more Pb UPD nanoclusters on top of the corresponding number of Pt nanoclusters, we have formation of one larger Pb UPD nanocluster which will not replicate the exact morphology of the underlying Pt deposit.

### 4. Conclusion

The presented study reveals several important results which are of broader significance for fundamental understanding of the UPD process on modified-bimetallic surfaces. They could be of general importance for catalyst monolayer synthesis and thin film deposition using SLRR of UPD monolayers [15,17,18]. At most positive underpotentials, \( 0.400 \text{ V} < \Delta E < 0.600 \text{ V} \) the UPD on PtSML/Au(111) does not start by decoration of Pt submonolayer/nanoclusters as one would expect from basic voltammetry of Pb UPD on Pt(111). Instead, the process starts by decoration of the defect sites on free Au(111) surface, Fig. 8a,b. Further UPD process continues by formation of Pb UPD nuclei on Au terrace which is similar to Pb UPD on Au(111), Fig. 8c. This is an important result and suggests the apparent Pt nanoclusters passivity, which we attribute to the presence of Pt-OH layer at these underpotentials. The selective Pb UPD on Au terraces prior to deposition on the Pt nanoclusters provides a natural opportunity that can be exploited when designing the experimental conditions for deposition of full heteroepitaxial Pt monolayer on Au(111) using repetitive SLRR of Pb UPD layer by Pt ions [8,13]. The same is true if one considers design of true bi-metallic catalyst monolayers using repetitive SLRR steps each having different depositing metal ions.

The further UPD process continues by parallel completion of the UPD layer on top of Au portion of the surface and nucleation of Pb on top of Pt nanoclusters, Fig. 8d (\( 0.250 \text{ V} < \Delta E < 0.400 \text{ V} \)). More than one Pb nuclei forms on top of underlying Pt nanoclusters as indicated by S1-detail in the schematics of Fig. 8d. The ultimate stage of the Pb UPD process is the completion of the Pb UPD on top of Pt nanoclusters and densification of the UPD layer on Au terraces, Fig. 8e (\( 0.150 \text{ V} < \Delta E < 0.250 \text{ V} \)). The morphology of the full Pb UPD layer on PtSML/Au(111) does not replicate the exact morphology of the starting surface. The appearance of the fewer number but larger Pb nanoclusters is observed as compared to the starting population of Pt nanoclusters in PtSML/Au(111). This is the consequence of the merging of Pb UPD nanoclusters in the \( 2^{\text{nd}} \) layer due to their larger size as compared to the corresponding Pt nanocluster morphology, Fig. 8e-S2 detail. This work reveals important facts about single crystal surfaces modified by submonolayer of foreign noble metal in terms of their electrosorption properties. In deed, we believe that UPD on modified single crystal surface is not just a linear combination of the UPD process on each of the elemental constituents but represents a new system that deserves more attention in future studies of the UPD phenomenon.
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References