Electrocatalysis: Novel Synthetic Methods

Introduction

In the last several decades, the electrochemical synthesis and electrodeposition became the enabling fabrication methods behind the train of hi-tech enterprise [1,2]. There are many examples where electrochemical synthesis provides convenient if not “the only” approach to deliver the desired structures, materials or catalytic surfaces. In recent years, the scientific community has witnessed the numerous examples where electrochemical synthesis is used to grow multilayered metallic thin films and nano-structures [3,4,5], nano-scale metallic architectures [6.,8,9,10,11,12], and a high quality single crystal overlayers [13,14,15,16,17]. The most recent developments suggest that the electrochemical methods become an attractive fabrication route for catalyst synthesis for fuel cells and metal-air batteries [18,19]. These new applications make the future of the research in electrochemical material science a seemingly interesting and quite exciting endeavor.

The Metal Deposition via Surface Limiting Red-ox Replacement of Underpotentially Deposited Metal Monolayer

Recently, Brankovic et al. [20], have developed the deposition protocol which has been extensively used for synthesis of noble metal monolayers and catalyst materials [21,22,23,24,25,26]. The basic steps describing the concept behind this new deposition protocol are illustrated in Figure 1, [20]. The method is based on surface limiting red-ox replacement (SLRR) of underpotentially deposited (UPD) monolayer (ML) of metal M on substrate S(h,k,l) by more noble metal P. The amount of deposited metal P is controlled by reaction stoichiometry, structure and coverage of the UPD ML, (eq. 1) [27].

\[
\left( \theta_M \cdot \rho_{M}^{UPD} \right) \cdot \frac{M_{UPD}^{M} \cdot S(h,k,l) + \left( \theta_M \cdot \rho_{M}^{UPD} \right) \cdot \left( \frac{m}{p} \right) \cdot P_{solv}^{P^{p+}}}{P_{solv}^{P^{p^{+}}}}
\]

Here, m and p are the oxidation states of UPD metal M and more noble metal P. The factors, \( q_M \) and \( \rho_{M}^{UPD} \) are introduced to accurately express the amount of deposited metal P in ML units with respect to the areal density of the S(h,k,l) atoms. They are respectively the UPD ML coverage, and the packing density of M atoms in complete UPD ML with respect to the substrateS(h,k,l). The subscripts s and solv. indicate the physical state of the metal (solv. = solution phase and s = deposited). The stoichiometry of SLRR is also dependent on specific experimental conditions which can favor one or other oxidation state of the metal constituting the UPD ML. For example, in the case of Cu UPD ML, the Cu(I) ions are thermodynamically more favorable than Cu(II) if the presence of Cl\(^-\) is the only complexing anion in the near region of the electrode/solution interface [27].

If sequence A-E (Fig. 1) is repeated an arbitrary number of times, a multilayer homo- or heteroepitaxial films are obtained [16]. The thin film growth using this SLRR synthetic protocol can be completely automated with experimental apparatus for Electrochemical Atomic Layer Epitaxy (ECALE) developed by Stickney et al. [28]. The additional variations of the SLRR protocol was recently introduced by Dimitrov et al. for the thin film growth application [29]. In this approach the SLRR step in Figure 1C was combined with a short potential pulse representing a co-depositon of P and UPD ML of metal M on the substrate surface so that the “one cell, one solution” concept can be implemented.

The UPD represent a potential dependent adsorption process and the UPD ML coverage is controlled effectively down to a fraction of a monolayer [30]. According to stoichiometry of SLRR eq.(1), the same accuracy for deposition of metal P can be achieved as well. This important advantage gives the whole array of new opportunities for application of catalyst monolayer design and synthesis via SLRR of UPD ML.

The electrochemical driving force for redox replacement reaction (galvanic displacement) between the metal P and the UPD ML of metal M is the positive difference between the equilibrium potential of P metal and the equilibrium potential of M_{UPD}/S(h,k,l) at its coverage approaching a zero limit, \( q_{UPD}^{P^{p+}} \). This condition is defined as [31] (Figure 2):
\[ \Delta E_{\text{red-ox}} = \Delta E_{\text{EMF}}^0 - \Delta E_{\theta \to 0}^0 - \frac{RT}{F} \ln \left( \frac{a_{M^{n+}}}{a_{P^{p+}}} \right) > 0 \]  

Here, \( \Delta E_{\text{EMF}}^0 (\Delta E_{\text{EMS}}^0 = E_{P^{p+/P}}^0 - E_{M^{n+/M}}^0) \) represents the electromotive force for the bulk M and P galvanic couple at standard conditions (Figure 2). The \( \Delta E_{\theta \to 0}^0 \) represents the equilibrium potential of \( M_{\text{UPD}}/S(h,k,l) \) at \( \theta_{\text{UPD}} \to 0 \) limit at standard conditions (\( a_{M^{n+}}=1, a_{P^{p+}}=1 \), Figure 2), while the logarithmic term provides the correction for the departure from standard conditions. Inspection of eq.(2) offers the evidence that the driving force for the red-ox reaction can be modified by adjusting the activities of \( M^{n+} \) and \( P^{p+} \) ions in the immersing (displacement) solution. If there are no \( M^{n+} \) ions in the immersing solution, the logarithmic term in eq.(2) dominates the value of \( DE_{\text{red-ox}} \) (very large and positive), which means that extremely high overpotentials for nucleation could be achieved resulting in high nucleation rates and large nucleation density of the metal P on the substrate S.

Figure 1. The basic steps of the deposition method described in Ref.[20]. A-B: formation of M UPD ML on S(h,k,l), B: \( M_{\text{UPD}}/S(h,k,l) \) surface emersion from solution at certain potential ensuring the desired M UPD ML coverage of S(h,k,l). C: transfer to P\( ^{p+} \) containing solution at open circuit potential (OCP), D: red-ox or displacement reaction at OCP, E: final morphology of P/S(h,k,l) deposit.
The schematics of the thermodynamic entities and their relations determining the $\Delta E_{\text{red-ox}}$ eq. (2) for displacement reaction.

The gray lines are current – potential dependence for bulk M metal electrode and UPD ML of M on substrate S. The dark line is the current – potential dependence for bulk noble metal electrode. The terms from equation (2) are identified in the figure.

Figure 2

The images of deposit morphology of A) ~1 ML of Pd on Au(111) via SLRR of Cu$_{\text{UPD}}$/Au(111), reaction: Cu$_{\text{UPD}}$/Au(111) + Pd$^{2+}$ = Cu$^{2+}$ + Pd/Au(111), q = 1, q$^e$ = 1, m/p = 1, image size 200 nm x 200 nm, B) ~0.5 ML of Pt on Au(111) via SLRR of Cu$_{\text{UPD}}$/Au(111), reaction: Cu$_{\text{UPD}}$/Au(111) + Pt$^{4+}$ = Cu$^{2+}$ + 0.5Pt/Au(111), q = 1, q$^e$ = 1, m/p = 0.5, image size 320 nm x 320 nm, C) Pt submonolayer on Au (111), image size 150 nm x 150 nm. Images A and B are from Ref. [20], Image C is from Ref. [32]. Size of Pt clusters is ~3 nm. The achieved nucleation density $\sim 10^{13}$ cm$^{-2}$.

Depending on the combination of the M$_{\text{UPD}}$/S(h,k,l) and P$^{\text{Pt}}$ ions involved in the red-ox reaction, a different amount and coverage of P monolayer deposit is formed. This is illustrated in Figure 3 using the example of Pd and Pt deposit obtained by displacement of Cu$_{\text{UPD}}$/Au(111). The deposit morphology varies from an atomic monolayer thin film to monolayer high nanoclusters with very narrow size distribution (Figure 3A-B).

Particularly interesting result in Figure 3 is the spatially uniform coverage of Pt nanoclusters on Au(111) shown in image B. This suggest that nucleation of the depositing metal (Pt) is independent on thermodynamically favorable nucleation sites on substrate surface such as steps for example. This is evident if one compares the morphology of Pt SML deposit on Au(111) obtained by electrodeposition at low overpotentials [32] (Figure 3C) and the morphology of Pt sub-ML and Pd ML deposits shown in Figure 3A-B. In the latter case, one can notice that Pt and Pd nanoclusters are equally distributed across the surface regardless the presence of surface steps where preferential nucleation and growth is typically found.
during electrodeposition process (Figure 3C). This fact represents one of the major advantages of this deposition protocol over the traditionally used ones for catalyst synthesis application. By manipulation of the experimental conditions for SLRR it was demonstrated that design and synthesis of different catalyst ML can be achieved [22,23], as well as sub-monolayers (SML) with different coverage and morphology [23,24,34], heteroepitaxial ultra thin films, and ultra thin film alloys [16,29,35].

**Spontaneous Noble Metal on Noble Metal Deposition (NMonNM).**

The spontaneous noble metal deposition on noble metal surface occurs when freshly prepared and clean noble metal electrode is immersed in the solution containing different noble metal ions. This phenomenon has been reported in various systems like Ru$^{2+}$/Pt(h,k,l) [36,37], Pt$^{4+}$/Ru(h,k,l,m) [38,39], Pd$^{2+}$/Ru(0001) [40], and Pd$^{2+}$/Pt(h,k,l) [41,42]. The morphology of the deposit varies from monolayer high nano-clusters to larger 3D structures. The spontaneous noble metal on noble metal (NMonNM) deposition occurs as result of an irreversible surface controlled red-ox reaction among depositing noble metal ions and noble metal substrate. The substrate surface in this reaction becomes oxidized by noble metal ions to form the certain type of surface oxide/hydroxide. The entire process is represented by following reaction [38]:

$$\frac{m}{n} P^{n+} + S^0(h,k,l) + mH_2O \rightarrow \frac{m}{n} P^0_{dep} + [S^{m+}]_{OH}^{-} + mH^+$$  \hspace{1cm} (3)

where, \( P^{n+}, P^0, S^{m+} \) and \( S^0(h,k,l) \) are respectively, the noble metal ions, the noble metal deposit, the substrate in the surface hydroxide and the noble metal substrate. The conductive nature of Ru-oxide/hydroxide and ability to form more than one oxide/hydroxide monolayer without hindering the electron transport across the interface has been discussed as the reason for spontaneous formation of multilayer Pt and Pd deposits on Ru (0001) surface [38,40]. The thermodynamic driving force for NMonNM deposition can be expressed in terms of difference between the equilibrium potential of noble metal electrode in contact with its ions in the solution and the equilibrium potential for oxidation of the noble metal substrate [38,40];

$$\Delta E_{red-ox} = \Delta E_{P^{n+}/P^0} - \Delta E_{[S^{m+}]_{x}[OH]_{y}/S^0} > 0$$  \hspace{1cm} (4)

According to eq.(4), the change in concentration of the ions of depositing noble metal, or pH of the solution alters the effective driving force for spontaneous NMonNM deposition. This fact is conveniently used to achieve different noble metal nucleation densities, regime of nucleation, and deposit morphology (Figure 4). The NMonNM deposition offers advantage over the existing deposition methods due to the fact that 2D morphology of depositing noble metal is easily achieved without significant control of the deposition process (simple timmed immersion). The example of this advantage is illustrated in Figure 4 by comparison of ~1ML Pt/Ru(0001) deposit obtained by potentiostatic deposition, and ~0.7 ML Pt/Ru(0001) and 0.4 ML Pt/Ru(1010) obtained by spontaneous NMonNM depostion, Figure 4A-C.
Morphology of the Pt deposit on Ru(1010) (A) and Ru(0001) (B and C). The spontaneous NMonNM deposition is used in image (A) and (B) [33], and the potentiostatic deposition is used in image (C), h=30 mV. The depositing solution was 10^{-2} \text{ M} \text{PtCl}_6^{2-} + 10^{-2} \text{ M} \text{HClO}_4. The nucleation density in (A) and (B) is approximately \sim 500 times higher then in (C). (A) image size; 280 x280 nm, 2D, \sim 3 \text{ nm} \text{Pt clusters}, (B) image size; 130 x 130 nm, 2D, \sim 5 \text{ nm} \text{Pt clusters}, and (C) image size; 115 x 115 nm, 3D, \sim 10-15 \text{ nm} \text{Pt clusters}.

The introduction of NMonNM deposition method has initiated applications as possible route to produce catalysts for fuel cells with improved performance [38,39,44]. Different experimental methods were used to characterize electrosorption characteristics and activity of these modified bi-metallic noble metal surfaces for different reactions [39,43,45]. These efforts has led to the design and characterization of one of the most efficient catalysts know today for polymer electrolyte membrane fuel cell anodes [46,4,48].

Future Directions

The future prospect of the catalyst monolayer synthesis using metal deposition via SLRR reaction or NMonNM deposition techniques is quite exciting. Different variations of these methods could be applied in order to better control morphology of the catalyst monolayers and their activity [49]. For example, the SLRR deposition guided by the presence of organic phase adsorbed on the surface with UPD monolayer is one approach that deserves attention [50]. The concept is based on idea of spatially controlling the nucleation sites for catalyst monolayer clusters and their shape evolution by introducing an organic phase on the electrode surface. The example of Pt ML deposits obtained using this approach is shown in Figure 5. The 4,4'-bipyridine, adsorbed on CuUPD/Au(111) surface and serving as a template is shown in Figure 5A. As one can see, the 4,4'-bipyridine forms a rippled layer with hexagonal lattice on CuUPD/Au(111) surface. The nearest neighbor distance of the hexagonal lattice of the adsorbed 4,4'-bipyridine phase is 1.5 nm, while the average width and periodicity of the ripples is 3.5 nm. After red-ox replacement of CuUPD ML by Pt^{4+} through the 4,4'-bipyridine phase the Pt deposit formed on Au(111) is shown in Figure 5B and C [51]. The presence of adsorbed bi-pyridine phase has an obvious effect on the shape and orientation of deposited Pt nanoclusters (compare Figure 5B and C with Figure 5D). The average width of the Pt clusters is approximately the same (~3.2 nm) as the periodicity of bi-pyridine ripples shown in Figure 5A, (~3.5 nm). The elongated shape of Pt clusters and their propagating direction replicate the arrangement and symmetry of bi-pyridine ripples. These observations do indicate that adsorbed organic phase serving as template has decisive influence on nucleation and growth of Pt deposit during SLRR reaction.
Figure 5. The STM images of: A) 4,4'-bipyridine layer adsorbed on Cu_{UPD}/Au(111), E=-0.5 V vs. SCE in 0.1 M HClO₄, image size: 30x30 nm, B) Pt on Au(111) after SLRR of Cu UPD ML by Pt⁴⁺ through the 4,4'-bipyridine adlayer, image size: 100x100 nm C) Same as in B, image size 30x30 nm, D) Pt deposit on Au(111) after SLRR of Cu UPD ML by Pt⁴⁺, no organic template is present during SLRR, In images A, model of 4,4'-bipyridine is shown in upper left corner. In images A, B, C, lower right angle, the cartoons of the corresponding structures are shown.
References

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<tr>
<td><strong>Dr. Stanko Brankovic</strong></td>
</tr>
<tr>
<td>Electrical and Computer Engineering Department, Chemical and Bimolecular Engineering Department, and Chemistry Department, Houston, USA</td>
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