Water Structure at the Multilayers of Palladium deposited at nanostructured Au electrodes

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Dedicated to Professor Juan Feliu on the occasion of his 70th birthday and in recognition of his outstanding contributions to electrochemistry

Abstract

In situ ATR-SEIRAS experiments were carried out to describe water structure at the surface of multilayers of Pd modified nanopatterned gold film electrodes in contact with aqueous 0.1 M HClO₄ solution. The results show that the surface water becomes more ordered when the thickness of the Pd film increases. The “ice-like water” band becomes stronger and for the electrode with 5 ML Pd@Au, the ratio of “ice-like water” to “liquid-like water” becomes larger than that in bulk water. Concomitantly, the population of “monomers” or small water clusters diminishes. All surface water bands increase when hydrogen adsorption takes place. The bending band corresponding to “monomers” or “multimers” water is observed chiefly at the potentials of hydrogen adsorption.

Keywords: ATR-SEIRA, water structure, palladium multilayers

1. Introduction

In an “opinion” article Juan Feliu wrote recently: “In summary, the future tasks should involve the understanding of role of water at the interfaces as a fundamental molecular species. It is not only important that the solid is well controlled, we need to control dynamics in the solution side. I believe that this challenge will be the main issue of Physical Electrochemistry

and Electrocatalysis in the future.” [1] In response to this challenge, the present paper describes surface enhanced IR absorption spectroscopy (SEIRAS) studies of water structure at multilayers of Pd deposited at nanopatterned Au film (x ML Pd@Au). There is a lot of interest in understanding the catalytic properties of these materials. They were extensively investigated by Feliu and coworkers [2], Kiebler and Kolb [3-8], Uasaki et al. [9-10], Chen et al. [11], and Roudgar and Gross [12-13]. These studies demonstrated that thin film of Pd at Au display interesting catalytic properties. They also provided information concerning the structure and stability of these thin film materials. The DFT calculations [12-13] related the catalytic properties of thin film Pd electrodes to changes in their electronic structure. However, the question how electrocatalytic properties of Pd multilayers at Au depend on the surface water structure remains unanswered.

Recently we have applied SEIRAS to describe water structure at Au nanoparticles covered by 1 monolayer of Pd [14]. We have demonstrated that at the 1 ML Pd/@Au electrode, the surface water consists of a mosaic of ‘ice-like water’, “liquid-like water”, monomers or multimers and hydronium ions. The relative population of these structures depends on pH and hydrogen atom adsorption. In the present paper, we are expanding these studies to systems with multilayers of Pd deposited at Au (x ML Pd@Au) with the number of monolayers x changing from 1 to 5. We will then look at how the changes of the surface water structure affect the rate of hydrogen evolution reaction.

2. Experimental

2.1 Materials

Sodium perchlorate (NaClO_4), Hydrofluoric acid (HF), Ammonium fluoride (NH_4F), Ammonium chloride (NH_4Cl), Sodium sulfite (Na_2SO_3), Sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), Sodium tetrachloroaurate(III) hydrate ($\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$), were purchased from Alfa Aesar and used directly without further purification. All aqueous solutions were prepared with Milli-Q (Millipore, Bedford, MA) ultrapure water (18.2 M Ω cm).

2.2 Preparation of the multilayer Pd films on the nanostructured gold electrode

For SEIRAS experiments, the nanostructured gold film was deposited on a hemispherical

silicon prism surface using the electroless method developed by Osawa et al. [15]. The flat surface of the hemispherical silicon surface was immersed to 2% HF for ~2 min, and then in 40% NH_4F for another ~2 min to remove the oxide layer from the silicon surface and to terminate it with hydrogen atoms. Then a mixture of 0.014 M $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$, 0.15 M Na_2SO_3 , 0.05M $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, 0.05 M NH_4Cl , and 2% HF was used to deposit the gold film at 60 °C for a period of ~ 2min. The thickness of the gold film was controlled by the deposition time. After deposition, the gold film covered silicon prism was immersed in water avoiding the gold film drying and shedding.

The Pd film on the nanostructured gold surface was deposited by Adzic's method [16], which involves the replacement of Cu underpotentially deposited atoms (UPD) by a palladium salt. First, the gold film on silicon prism was immersed in a mixture of 1 mM CuSO_4 + 0.1 M H_2SO_4 to form a monolayer of underpotentially deposited Cu. The potential was controlled at 0.0 V vs Ag/AgCl for two minutes, to form a full monolayer of Cu on the Au electrode surface. The monolayer Cu coated Au electrode was then immediately immersed into 10 mM Na_2PdCl_4 solution for three minutes to completely replace Cu with Pd. To obtain multiple layers of Pd@Au, the repetitive UPD of a full monolayer of Cu at a Pd coated Au surface in 1 mM CuSO_4 + 0.1 M H_2SO_4 solution and subsequent displacement of Cu by Pd in 10 mM Na_2PdCl_4 solution were applied. We prefer to use this method rather than direct deposition of a known amount of Pd determined from the charge flowing to the electrode applied in Ref. [17]. In the direct deposition only first two layers have layer-by-layer structure. The layer-by-layer growth is not ensured for thicker multilayers Pd films [17]. Further the direct deposition was applied for a smooth well-defined electrode with precisely known surface area. In the present study, nanopatterned electrode with poorly controlled area was used. By using the layer-by-layer deposition, one controls extensive quantity such as potential of Cu UPD. In that way the result is not affected by the uncertainty of the surface area.

2.3 Electrochemical instrumentation and measurements

The electrochemical measurements were performed in all-glass three-electrode cells. The nanostructured gold films on the silicon wafer surface served as the working electrodes. The

Ag/AgCl (saturated KCl) electrode (Pine Research Instrumentation, NC) was used as the reference electrode, and a gold coil was employed as the counter electrode. Before each measurement, the cell was de-aerated by purging with argon (Linde Canada, Guelph, Ontario, Canada) for 30 minutes. An argon blanket was maintained above the electrolyte throughout the experiments to prevent the influx of oxygen.

2.4 SEIRAS measurements

SEIRAS experiments were performed using a Thermo Nicolet Nexus 8700 spectrometer (Madison, WI) with an all-glass three-electrode cell. The nanostructured gold film deposited on the silicon prism surface served as the working electrode. The SEIRA measures differential spectra defined as:

$$A = 1 - \frac{I}{I_0} \quad (1)$$

where I and I_0 are the single beam intensities of reflections at the sample and the reference potentials, $\Delta A = A(E) - A(+0.6)$ where $A(E)$ is the absorbance at the sample potential E and $A(+0.6)$ is the absorbance at the reference potential of +0.6 V vs Ag/AgCl. The sample spectra were collected for potentials E from +0.5 V to -0.2 V vs Ag/AgCl with 0.1 V interval. At each potential, 500 IR scans were added and averaged with the instrumental resolution of 4 cm⁻¹.

3. Results and Discussion

3.1 Electrochemical characterization

Figure 1. Cyclic voltammogram for the 2-5 ML Pd@Au electrode in 0.1 M HClO₄ recorded using sweep rate 50 mV s⁻¹.

Figure 1 shows cyclic voltammograms (CVs) for 2-5 ML Pd @ Au electrodes in 0.1 HClO₄ recorded at a scan rate of 50 mV s⁻¹. The CVs are in good agreement with the data published [2, 6, 17-19]. They correspond to the double layer region of these electrodes. The small and broad peak at ~0.3 V vs Ag/AgCl was assigned to OH adsorption/desorption [18]. The peaks between +0.05 and -0.2 V vs Ag/AgCl correspond to hydrogen adsorption (underpotential deposition (UPD)) or hydrogen absorption by Pd film. STM studies [7-8, 17] and DFT calculations [12-13] demonstrated that up to 2 ML deposition of Pd has pseudomorphic character. The three-dimensional deposition takes place when the thickness of the Pd film exceeds 3 ML. Consequently, no hydrogen absorption is observed for 1 ML and 2 ML Pd films and hydrogen absorption begins for thicker films. The increase of hydrogen peaks observed for films thicker than 2 ML may be attributed to hydrogen absorption. The negative current at $E < -0.2$ V vs Ag/AgCl is due to hydrogen evolution.

3.2 SEIRAS studies of water at multilayers of Pd@Au in the O-H stretching region

Figures 2 plots $\nu(\text{OH})$ bands recorded at x ML Pd@Au electrodes with the number of Pd monolayers x ranging from 2 to 5. These are potential difference spectra that plot the difference between absorbance at a sample potential E and the reference $E = +0.6$ V vs Ag/AgCl. The shape of the spectra changes when the number of Pd monolayers increases and when the electrode

potential becomes more negative. The bands in the spectra of Figure 2 are positive indicating that the spectra become more intense when potential becomes negative. This behavior indicates that either density of surface water increases, or the orientation of water molecules becomes more favorable for the absorption of IR photons when potential becomes more negative. SEIRAS measures spectra corresponding to a few monolayers of water at the surface. Therefore they probe water both in specifically adsorbed ions and ions in the outer Helmholtz plane (oHp). Perchlorate ions are weakly hydrated. Consequently, the increase of water band intensity when potential moves in the negative direction may reflect diminishing population of perchlorate ions and increasing population of strongly hydrated hydronium ions.

Figure 2. Potential difference spectra of water at the 2-5 ML Pd on Au film electrode in 0.1 M HClO_4 calculated by using the single-beam spectra at 0.6 V vs Ag/AgCl as the reference.

To analyze changes in the band shape quantitatively, Figure 3 compares the ATR spectrum of bulk water (red curve) to the SEIRAS spectrum at the 5 ML Pd@Au electrode at $E=-0.2$ V vs Ag/AgCl (black solid line). Note that in the ATR configuration the escape depth of the evanescent wave is about one quarter of its wavelength. The wavenumbers ~ 3400 cm^{-1} correspond to the wavelength ~ 3000 nm and the escape depth corresponds to ~ 750 nm. These numbers show that the amount of surface water is negligible in comparison to the amount of bulk water probed by the ATR spectra. This SEIRAS spectrum has the most intense bands and hence its shape is predominantly determined by absorbance at the sample potential. The $\nu(\text{OH})$ band of water is very broad and its envelop contains several sub-bands. Fourier self-deconvolution (FSD) procedure [20], which narrows the bands, could be used to reveal the presence of sub-bands in a broad spectrum. The dashed red line in Figure 3 plots the FSD of the ATR spectrum. It reveals the presence of three bands at 3220, 3390 and 3610 cm^{-1} . The bands at 3220 and 3390 cm^{-1} correspond to water molecules in a network of hydrogen bonds (network water). The band at 3220 cm^{-1} is referred to as the “ice-like water” band and corresponds to OH stretching vibration of stronger hydrogen bonds. The band at 3390 cm^{-1} is called the “liquid-like water” band and corresponds to stretching vibrations of water molecules forming a network of weaker hydrogen bonds. The band at 3610 cm^{-1} corresponds to water molecules with a disturbed network of hydrogen bonds (monomer or multimer water molecules [21-25]).

Figure 3. The top red curve is the ATR spectrum of bulk water, the purple spectrum below (dashed red) is its FSD. The black line plots the SEIRAS spectrum of water at the 5 ML Pd@Au

at -0.2 V vs Ag/AgCl. The bottom (black dashed) spectrum is the FSD of the SEIRAS spectrum.

The SEIRAS spectrum is similar to the ATR spectrum. However, there is an additional band at $\sim 3480\text{ cm}^{-1}$ which indicates the presence of “liquid-like water” with a more disturbed network of hydrogen bonds or adsorbed water molecules with hydrogen atoms close to the metal surface [26]. The SEIRAS spectrum for 5 ML Pd@Au is quite similar to the SEIRAS spectrum of a film of Pd chemically deposited at a silicon prism [27].

Figure 4 compares SEIRAS spectra measured at $E = -0.2\text{ V}$ vs Ag/AgCl for 1 to 5 ML Pd films. The spectra for films with 1 to 3 ML of Pd are very similar. This behavior is consistent with literature which demonstrated that a transition from pseudomorphic to three-dimensional growth takes place when the thickness of Pd film exceeds 2 -3ML [8, 12-13, 17].

Figure 4 Potential difference SEIRA spectra of water at the 1-5 ML Pd@Au in the $\nu(\text{HOH})$ region in 0.1 M HClO_4 at $E = -0.2\text{ V}$ vs Ag/AgCl.

Indeed, significant changes are observed for films with 4 or 5 ML of Pd. These changes include an overall increase of the “ice-like water” band at $\sim 3220\text{ cm}^{-1}$ and “liquid-like water” band at $\sim 3480\text{ cm}^{-1}$. Figure 5 plots variation of band intensity of “ice-like water” band, “liquid-like water” band and multimer/monomer water band at 1-5 ML Pd@Au film in 0.1 M HClO_4 as a function of the electrode potential. To avoid uncertainty of deconvolution of broad bands,

Figure 5 plots intensities read from the raw spectra at wavenumbers corresponding to maxima in the FSD spectrum. Each spectrum was measured at least three times using freshly prepared electrode. Each time independent base line correction was applied. The reported intensities are the average of these independent measurements. The uncertainty of the background correction is reflected in the error bars included in the reported data. The intensities of “ice-like water” and “liquid-like water” bands change little with potential till the onset of hydrogen evolution at -0.2 V vs Ag/AgCl. At these potentials, the intensities increase for all Pd coverages. For Pd films with 1 to 3 ML intensities of these two bands change little with coverage of Pd. The dependence on the coverage is pronounced for films with 4 and 5 ML of Pd. In contrast to behaviors of “ice-like water” and “liquid-like” water bands, the intensity of the multimer/monomer band at $\sim 3610\text{ cm}^{-1}$ (Figure 5C) depends strongly on potential. It increases when E becomes more negative. At $E > 0.0\text{ V}$ vs Ag/AgCl, the intensities of this band are higher for films with thickness less than 3 ML than for films with 4 ML and 5 ML of Pd.

Figure 5 Variation of band intensity of (A) “ice-like water” band at $\sim 3240\text{ cm}^{-1}$, (B) “liquid-like water” band at 3470 cm^{-1} and (C) multimer/monomer water band at $\sim 3620\text{ cm}^{-1}$ at 1-5 ML Pd@Au film in 0.1 M HClO_4 as a function of the electrode potential. 1 ML: red circles, 2 ML: magenta rectangles, 3 ML: orange diamonds, 4 ML blue rectangles, and 5 ML: black stars.

Small changes of the surface enhancement of the electric field of the photon between samples with different Pd coverage may affect bands intensities measured at electrodes with different Pd coverage. The variation of surface enhancement is removed when the analysis is based on R_{network} and $R_{\text{multimere}}$ values. The structure of water can be quantified by calculating

R_{network} defined as a ratio of absorbance at 3220 cm^{-1} (A_{3220}) to absorbance at 3390 cm^{-1} (A_{3390}):

$$R_{\text{network}} = \frac{A_{3220}}{A_{3390}} \quad (2)$$

The ratio of monomers to “liquid-like water” is given by the ratio of absorbance at 3610 cm^{-1} (A_{3610}) to absorbance at 3390 cm^{-1} (A_{3390}):

$$R_{\text{multimer}} = \frac{A_{3610}}{A_{3390}} \quad (3)$$

It could be used to estimate changes in the population of monomers or multimers of water molecules relative to the population of “liquid-like water” [23, 25, 28-29]. The values of R_{network} are plotted in Figures 6A. In bulk water $R_{\text{network}}=0.67$. The values of R_{network} progressively increase with the increasing number of monolayers. For films with 1 and 2 ML Pd, the values of R_{network} are much lower than for bulk water, indicating that at the pseudomorphic films the surface water is more disordered than in the bulk. For films with 3 and 4 ML Pd, R_{network} attains value close to the value for bulk water, suggesting that fractions of “ice-like water” and “liquid-like water” at the surface are comparable to that in the bulk. For electrode with 5 ML Pd, R_{network} for surface water is higher than in the bulk. Surface water is more ordered than water in the bulk. The values of R_{network} display a shallow minimum at $E \sim 0.1 \text{ V}$ vs Ag/AgCl. It corresponds to the potential of a minimum order of water molecules at Pd surface. The potential of zero charge of the electrode with 1 ML Pd@Au is equal to -0.11 V vs Ag/AgCl [14, 30]. Therefore, the minimum order of surface water is observed at a potential $\sim 0.2 \text{ V}$ more positive than E_{pzc} , just before the onset of OH adsorption.

Figure 6. Variation of (A) R_{network} and (B) R_{multimer} in 0.1 M HClO_4 as a function of applied potential at different Pd@Au layers. 2 ML: red circles, 3 ML: magenta rectangles, 4 ML: blue triangles and 5 ML: black diamonds.

The parameter R_{multimer} calculated from the ATR spectrum for bulk water is equal to 0.17. Figure 6B shows that for water at Pd@Au electrode surfaces, the R_{multimer} values are much higher than 0.17, indicating that surface water contains much more multimers/monomers than bulk water. In contrast to R_{network} , the values of R_{multimer} progressively increase when potential becomes more negative and decreases with coverage of Pd. For the electrode with 5 ML Pd, it attains the value of bulk water at $E=0.3 \text{ V vs Ag/AgCl}$. When the hydrogen bond network becomes stronger and the surface water becomes more ordered, the population of monomers or small clusters of water molecules diminishes at the surface.

3.3 SEIRAS studies of water at multilayers of Pd@Au in the H-O-H bending region

The IR spectra in the $\delta(\text{HOH})$ region provide further information about the properties of surface water. The four panels in Figure 7 plot SEIRAS spectra of water molecules in the

bending mode region for the x ML Pd@Au electrodes with numbers of Pd monolayers ranging from 2 to 5. They show two bands, one at ~ 1675 cm^{-1} and a second at ~ 1600 cm^{-1} , seen at more negative potentials. The SEIRAS spectra are quite different than the ATR spectrum of bulk water (top curves in Figures 7). The FSD analysis of spectra at $E=-0.2$ V Ag/AgCl (bottom curves in Figures 7) show that the broad band at ~ 1670 cm^{-1} consists of two sub-bands centered at ~ 1700 and ~ 1660 cm^{-1} . The band at ~ 1700 cm^{-1} has been observed by Osawa et al. [31] at Pt(111) and Garcia-Araez et al. [26] at Au(111) in HClO_4 solutions and was assigned to hydronium ion following Wagner and Moylan [32] and Chen et al. [33]. The band at ~ 1590 cm^{-1} was assigned to “monomer” water. The band at 1660 cm^{-1} was assigned to network water.

Figure 7 Potential difference spectra of water at the 2-5 ML Pd on Au film electrode in 0.1 M HClO_4 calculated by using the single-beam spectra at 0.6 V vs Ag/AgCl as the reference. The top curves are ATR spectra of bulk water and the bottom dashed line is the FSD result of the SEIRA spectra at $E=-0.2$ V vs Ag/AgCl.

To discuss these spectra, Figures 8 A to C plot intensities of the monomer/multimer band at 1600 cm^{-1} (Figure 8A), the network water band at 1660 cm^{-1} (Figure 8B) and the hydronium ion band at 1700 cm^{-1} (Figure 8C) for the four electrodes, as a function of the applied potential. The data show that the monomer/multimer water band is only observed at $E < 0.1$ V vs Ag/AgCl and decreases significantly for the electrode with 5ML of Pd. The network and hydronium bands intensities are higher for that electrode as well. These behaviors are consistent with the increased ordering of surface water shown by spectra in the stretching region. In summary, the SEIRAS spectra recorded at electrode with the increasing number of Pd monolayers demonstrated that the surface water becomes more ordered and the fraction of monomer/multimer water molecules diminishes when the thickness of Pd increases.

Figure 8. Variation of band intensity of (A) monomer water band ($\sim 1590\text{ cm}^{-1}$), (B) network water band ($\sim 1660\text{ cm}^{-1}$) and (C) hydronium ion band ($\sim 1700\text{ cm}^{-1}$) at 2-5 ML Pd@Au in 0.1 M HClO₄ as a function of the electrode potential. 2 ML: red circles, 3 ML: magenta rectangles, 4 ML blue rectangles and 5 ML: black diamonds.

Figure 9 (A) Dependence of intensity of the hydronium ion band (A_{1700}) at $E = -0.2\text{ V}$ vs Ag/AgCl, just before the onset of hydrogen evolution, on the number of Pd monolayer. Relation between the hydronium ion band (A_{1700}) intensity at $E = -0.2\text{ V}$, and the hydrogen evolution exchange current (j_0) taken from Ref. [4].

Figure 9A plots the hydronium ion band intensity (A_{1700}) at $E (-0.2\text{ V})$, just before the onset of hydrogen evolution, as a function of the number x of Pd monolayers. It shows that the intensity of the hydronium band increases with the thickness of the Pd film. Small scatter of the experimental points is related to the irreproducibility of the surface enhancement at the

nanopatterned films. Figure 9B plots dependence of the A_{1700} band intensity on the exchange current of hydrogen evolution. It shows that the intensity of A_{1700} band is proportional to hydronium ions density present at the surface. The data indicate that increase of the current density with the thickness of the Pd film correlates well with the increase of the surface concentration of hydronium ion. This correlation suggests that in the hydrogen evolution reaction electrons are transferred to the adsorbed hydronium ions.

Conclusions

At x ML Pd/@Au electrodes, the surface water consists of a mosaic of ‘ice-like water’, ‘liquid-like water’, monomers or multimers and hydronium ions. The relative population of these structures depends on pH (see Ref. [14]), hydrogen atom adsorption and the thickness of Pd film. For electrodes with the number of monolayers less than 5, it is less ordered than water in the bulk. However, the order increases with the thickness of the Pd film and for the electrode with 5 ML Pd@Au, the surface water is more ordered than bulk water. The ‘ice-like water’ band becomes stronger and the ratio of ‘ice-like water’ to ‘liquid-like water’ becomes larger than that in bulk water. Concomitantly, the population of ‘monomers’ or small water clusters diminishes. All surface water bands increase when hydrogen adsorption takes place. The bending band corresponding to ‘monomers’ or ‘multimers’ is observed chiefly at potentials of hydrogen adsorption.

Figure 10. Variation of hydrogen evolution exchange current (j_0) vs R_{network} (red circles, left y-axis) and hydrogen evolution exchange current (j_0) vs R_{multimer} (blue rectangles, right y-axis).

The number of Pd layers was marked in the figure. The data of hydrogen evolution exchange current density were taken from Ref. [4].

The SEIRAS studies provided a tremendous amount of information about the structure of surface water at xM LPd@Au electrodes. This knowledge could be used to correlate the rate of hydrogen evolution at these electrodes to parameters characterizing water structure such as R_{network} (a measure of “ice-like” water population) and R_{multimer} (a measure of “monomer/multimer water population). Figure 10 shows the relationship between these two parameters at $E = -0.2$ V vs Ag/AgCl corresponding to the onset of hydrogen evolution reaction and the exchange current density of hydrogen evolution, taken from the paper by Kibler [4]. Contrary to expectations, the rate of hydrogen evolution increases when the surface water becomes more ordered. This good correlation indicates that the up-shift of the d -band center and increased contribution of d -bands to the electronic structure of the metal substrate assist in the ordering of the surface water as well [12-13].

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