Reactivity of monolayers and nano-islands of palladium on Au(1 1 1) with respect to proton reduction

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Abstract

Electrochemical reactivity regarding hydrogen reduction was studied at epitaxially grown Pd monolayers and sub-monolayers on Au(1 1 1) in 0.1 M HClO$_4$ solution. The rate of hydrogen evolution increases with decreasing numbers of layers, and it is considerably higher for sub-monolayers, i.e. the fewer Pd islands are on the surface the higher is the catalytic activity. No clear dependence of the reactivity on the ratio of Pd edge atoms to terrace atoms was found. Possible mechanisms explaining the experimental results are discussed.
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1. Introduction

Nano-scale effects in the catalytic properties of gold particles are well known, e.g. chemically inert gold turns catalytically active when the particle size is below 3–4 nm [1,2]. The existence of such size effects offers a new possibility of controlling reactivity by controlling the particle size.

Recently, it has been shown that single palladium nanoparticle supported on Au(1 1 1) exhibit higher electrocatalytic reactivity regarding hydrogen evolution reaction as compared to bulk palladium [3–5]. Nano-scale and geometrical effects can explain the enhancement of the catalytic properties of nano-particles supported on foreign substrates. The geometrical so-called electronic effect arises due to strain in the lattice of the supported metal generated from the bigger lattice constant of the substrate [6–13].

One of the most investigated systems is palladium overlayers on Au(1 1 1) substrate. Palladium has high catalytic activities for many chemical reactions and the ability to absorb hydrogen. Kibler et al. [14] have shown that a monolayer of palladium electrodeposited on Au(1 1 1) has a higher reactivity regarding formic acid oxidation as compared to Pd(1 1 1). The electrocatalytic properties of thin Pd overlayers on Au (h k l) have been investigated for oxygen reduction as well as for the oxidation of methanol, formaldehyde and adsorbed CO. The main question still concerns the origin of the electrocatalytic enhancement of overlayers. Hammer and Norskov [6] have reported that the *d*-band position may be a crucial parameter for the adsorption behavior. The *d*-band position can be changed due to "expansion" or "compression" of the lattice constant. Nørskov et al. [15,16] have reported a *d*-band upward shift of approximately 0.35 eV for a pseudo-morphic Pd monolayer on Au(1 1 1). To better understand the electro catalytic enhancement due to electronic effects experimental systems with extended surfaces are needed. On one hand, by investigating extended surfaces the nano-scale effects are negligible and the electronic effect can be investigated separately. On the other hand, investigations of monoatomic high Pd islands on Au(1 1 1) with different size distributions can reveal the influence of the size-effects on electrocatalysis.

In this study, the reactivity regarding hydrogen evolution at palladium monolayers and monoatomically high nano-islands on Au(1 1 1) was investigated in 0.1 M HClO$_4$ solution as a function of the palladium coverage. The electrocatalytic properties regarding hydrogen evolution reaction are significantly affected by the quantity of palladium coverage. Sub-monolayers coverage demonstrate higher reactivity compared with monolayer palladium on Au(1 1 1). In the case of sub-monolayers the origin of the electrocatalytic enhancement regarding hydrogen evolution reaction is explained with a simple physical model.

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2. Experimental

The electrochemical reactivity measurements were carried out in a standard glass cell with a potentiostat/galvanostat PG 310 (HEKA Electronic). All images were obtained in the constant current mode. STM tips were etched from Pt/Ir wire (atomic ratio 90:10, 0.25 mm in diameter) and insulated with an electrophoretically deposited lacquer. The used working electrodes (substrates) were made from evaporated gold films on tempax glass (Metallhandel Schroer GmbH). The film structure of the samples was as follows: 250 nm gold, 2.5 nm chromium layer and 1.1 mm borosilicate glass. All of them were of square size with 11 mm width. Prior to the measurements the gold surface was flame annealed and cooled to ambient temperature in a nitrogen stream. This resulted in several hundred nano-meter wide terraces, which are atomically flat and (1 1 1)-oriented.

A gold spiral was used as counter electrode. In order to get it cleaned, prior to measurements the electrode was flame annealed. In the case of reactivity measurements in standard glass cell the reference electrode was Mercury/Mercury Sulfate/0.1 M H_2SO_4 (Schott B 3610). An oxidized gold wire was used as a reference electrode in the electrochemical STM-cell. The gold wire was cleaned by flame annealing and prepared by anodic oxidation in 0.1 M $HClO_4$. The oxidizing was stopped when the gold wire becomes dark-brown colored.

Palladium monolayers on Au(1 1 1) were prepared in standard glass cell as follows: the gold electrode was contacted to a 0.1 M $HClO_4$ solution containing 0.5 mM $Pd(NO_3)_2$ at 1 V where no Pd deposition took place and, then, the electrode potential was swept to different deposition potentials varying from 0.75 to 0.5 V by 50 mV s^{-1} depending on the desired Pd coverage. In the case of lower sub-monolayer coverage the deposition was carried out in the electrochemical STM cell with potential pulses. Varying the height and the duration of the potential pulse different morphology of the Pd deposits were obtained. Thus, narrow size distributions of the deposited Pd monoatomic high nano-islands were achieved. The potential pulse deposition technique gives the possibility to deposit samples with the same size distribution but different coverage. Therefore, the influence of the gold free surface can be investigated. In other to obtain the morphology parameters the electrode surfaces were characterized with *in situ* STM images. The morphology analysis of the STM images such as Pd coverage, island perimeter distribution, total island perimeter length and the number of Pd islands were evaluated with scanning probe microscope software WSxM 4.0 Develop 8.5 (Nanotec Electronica S.L.). The number of Pd edge (N_e) and terrace (N_t) atoms was calculated from the Pd coverage and the total perimeter length.

After the Pd deposition the electrode was rinsed with oxygen free Milli-Q water and then transferred to another cell for the reactivity measurements in 0.1 M $HClO_4$ solution. The Pd coverage was obtained by three independent measurements. In the first one, the coverage was calculated from the charge transferred by the deposition cathodic current. In the second measurement the coverage was estimated from the *in situ* STM images. In the last third case the Pd coverage was derived from the hydrogen adsorption charge in a cyclic voltammogram taken before the reactivity measurements. The reactivity measurements were performed only for the samples with less then 5% difference for the Pd coverage calculated from all three mentioned above methods. Galvanostatic pulse transients in 0.1 M $HClO_4$ were used for the reactivity measurements. The applied galvanostatic pulse duration and the sampling rate were 60 ms and 200 kHz, respectively. The measured potentials were corrected for the IR drop. For each set of transient measurements Tafel plots were obtained.

The solutions were prepared from $HClO_4$ (Merck, Suprapur), and $Pd(NO_3)_2$ (MaTecK) with Millipore-Milli-Q water (18.2 MΩ cm, 2 ppb total organic carbon). All solutions were oxygen free by purging with nitrogen for at least 20 min. During the measurements nitrogen was passed over the solution. All measurements were performed at room temperature. Hereafter, in this article all potentials are given versus RHE.

3. Results

The first two cycles of a typical cyclic voltammograms (CVs) for Au(1 1 1) electrode in 0.5 mM $Pd(NO_3)_2$ + 0.1 M $HClO_4$ solution are shown in Fig. 1. The calculated charge density of the cathodic peak at 0.68 V from the first cyclic voltammogram is 420 μC cm^{-2}, corresponding almost perfectly to the deposition charge of a full Pd monolayer on Au(1 1 1) (1 ML = 423 μC cm^{-2}). The peak at 0.68 V from the first CV is not observed in the second one. The reason is that this peak is characteristic only for the deposition of the first monolayer Pd. The first monolayer Pd is deposited in the first CV and in the second CV the further Pd deposition occurs. The cathodic current shoulders at potential around 0.2 V can be attributed to hydrogen adsorption on the deposited palladium overlapped with further Pd bulk deposition. Also, at the negative potential values the hydrogen evolution reaction appears in addition to Pd deposition. In the second cycle the peak is better resolved because of the larger amount of deposited Pd. The peaks in the positive potential sweep are due to desorption of the adsorbed hydrogen from the palladium surface. The peaks in both CVs
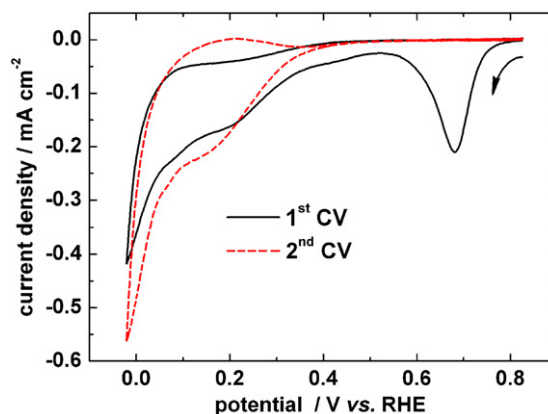

Fig. 1. Cyclic voltammograms for Au(1 1 1) in 0.1 M $HClO_4$ with 0.5 mM $Pd(NO_3)_2$ solution. Initial potential 0.825 V vs. RHE. Sweep rate 50 mV/s. The measured equilibrium potential for Pd/Pd^{2+} in that solution is 0.8 V.