



Hydrogen evolution on Au(111) catalyzed by rhodium nanoislands

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ABSTRACT

Pronounced catalysis of hydrogen evolution reaction (HER) by rhodium nanoislands spontaneously deposited on Au(111) has been observed. Different Rh/Au(111) nanostructures were characterized ex situ by both height and phase imaging AFM. The most pronounced catalytic activity for HER in 0.5 M H₂SO₄ was obtained for 50% Rh coverage. This is ascribed to the suitable size of Rh nanoislands and to the electronic modification of Rh deposit by Au(111) substrate.

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1. Introduction

Significant catalysis of hydrogen evolution reaction (HER) on different Pd/Au(111) nanostructures obtained by different methods of Pd deposition on Au(111) substrate has been reported in recent years [1–5]. These reports have focused our attention on the other metals (Me) from platinum group expecting that the activity for HER of such Me/Au(111) nanostructures might be comparable or higher than that of Pd/Au(111). Indeed, a higher activity of Au(111) with Rh overlayer, even exceeding that of platinum has been theoretically predicted [6,7]. According to calculations in Ref. [6], such a high activity of Au(111) surface covered with Rh overlayer is related to the strong electronic effect, due to which both hydrogen adsorption and recombination are extremely fast, even faster than on pure Pt(111). Up to now there are no reported experimental data about the activity of Rh/Au(111) system toward HER.

Volmer–Weber or island growth of Rh on Au(111) without intermixing or Rh incorporation underneath of Au(111) surface has been observed by UHV STM at room temperature [8]. For rhodium electrochemically deposited on Au(111), Stranski–Krastanov growth, where the epitaxial growth of the first monolayer is followed by the island growth is reported [9]. It has been shown that Me/Au(111) nanostructures obtained by a spontaneous metal deposition on the Au(111) substrate always follow the island growth mode [3,4,10–12]. Since that among other bimetallic surfaces, Pd/Au(111) nanostructures prepared in this way have shown the highest activity for HER so far [3,4], it was

a particular challenge to investigate different Rh/Au(111) nanostructures obtained by the same method and confirm their previously theoretically predicted even higher activity toward HER.

2. Experimental

Au(111) single crystal, 12 mm in diameter (MaTeck, Julich, Germany), with miscut lower than 0.1°, was prepared as described elsewhere [3,4]. Spontaneous deposition of Rh on Au(111) electrode was performed by immersion of the electrode at an open circuit potential into (1 mM RhCl₃·xH₂O + 0.5 M H₂SO₄) solution for the deposition times of 0.5, 1 and 3 min. A special care and a thorough cleaning are needed to avoid the impact of metal impurities on HER as pointed out in Ref. [13]. After each experiment the electrode was cleaned by repeated electrochemical polishing [4] in order to remove the traces of the deposit until clean Au(111) surface becomes fully recovered.

Obtained Rh/Au(111) nanostructures were characterized ex situ by tapping mode Atomic Force Microscopy (AFM) using Multimode Quadrex SPM with Nanoscope IIIa controller (Veeco Instruments, Inc.) with a commercial Veeco RFESP AFM probe (NanoScience Instruments, Inc.). Height AFM images which are sensitive to surface topography and phase AFM images which are sensitive to the surface chemical composition and independent of the topography were acquired simultaneously for each Rh/Au(111) sample. Coverage, representing a percentage of the Au(111) surface covered with the deposited Rh islands, was estimated from phase AFM images taken from different areas within each sample. Final image processing is described in details elsewhere [3,4].

The electrochemical characterization of Rh/Au(111) surfaces was performed by Cyclic Voltammetry (CV) in oxygen free 0.5 M H₂SO₄ solution using hanging meniscus method. CVs were recorded in the

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potential region from HER up to 1.0 V, after conditioning at -0.05 V for 15 min in order to reduce rhodium deposit to its metallic state. Polarization measurements for HER were performed in the potential region from 0.0 V to -0.4 V, after previous conditioning at 0.0 V for 15 min.

Solutions were prepared using $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (MaTech), suprapure H_2SO_4 (Merck), and Milli-pure water. Sulfuric acid solutions were deaerated by 99.999% N_2 (Messer) before each measurement. The counter electrode was Pt wire, and the reference electrode was Ag/AgCl , 3 M KCl . All measurements were performed at room temperature.

3. Results and discussion

3.1. Height and phase AFM images of Rh/Au(111)

Representative height and phase AFM images of Rh/Au(111) nanostructures providing the insight into the surface topography and chemical contrast between Au(111) substrate and rhodium deposit are given in Fig. 1. Images obtained for the lowest deposition time of 0.5 min show distinctive Rh islands mostly 2–2.5 nm wide and one monolayer high (the step height for Rh(111) is 0.22 nm) with the coverage of (35 ± 2) %. These images are not presented since they display similar features like ones obtained for 1 min deposition, which are shown in Fig. 1a and b. Due to the higher Rh coverage and larger Rh islands, these images display more pronounced features. Analysis of surface topography AFM image, Fig. 1a, shows that Rh islands are preferentially deposited on steps and randomly distributed on terraces. Islands are mostly monolayer high and 5–10 nm wide with an average distance of 7 nm. Few two-monolayer high islands are observed on steps. On phase AFM image, Fig. 1b, Rh islands which are densely agglomerated along steps as well as ones deposited on terraces are clearly highlighted and distinguished from Au(111) substrate. The overall estimated coverage is (50 ± 2) %.

For the deposition time of 3 min, Fig. 1c and d, Rh islands are agglomerated into wider domains on terraces and up to a full coverage along steps, giving the overall coverage of (90 ± 2) %. Yet, the individual 5–10 nm wide islands can still be recognized in the phase image. When

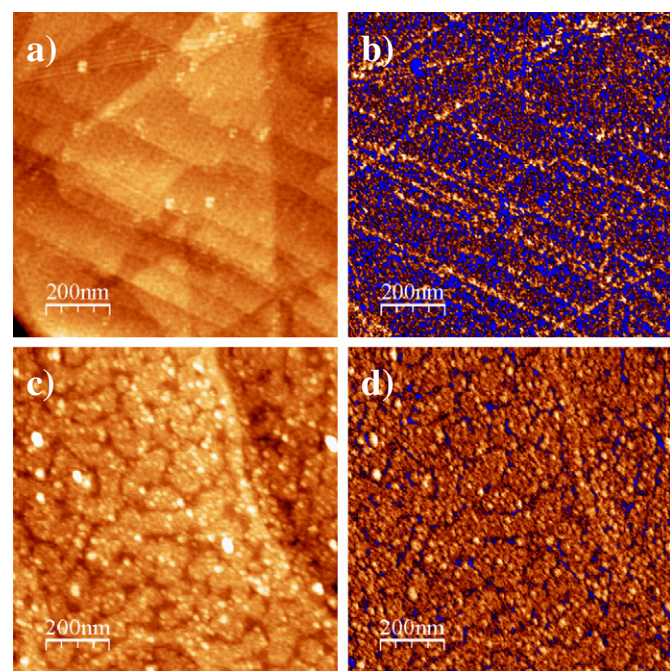


Fig. 1. Top-view AFM images (1×1) μm^2 of different Rh/Au(111) nanostructures showing: surface topography (left column) and corresponding phase images (right column). Images are obtained after spontaneous Rh deposition for: a) 1 min, z-range 2.5 nm; b) 1 min, z-range 0.86°; c) 3 min, z-range 2.0 nm; and d) 3 min, z-range 1.65°.

the threshold in phase images was set at the height which corresponded to one Rh monolayer, than the surface coverage which was estimated to be approx. 15% referred to the islands two or more monolayer high.

3.2. Cyclic voltammetry of Rh/Au(111)

Rh/Au(111) nanostructures were electrochemically characterized by cyclic voltammetry in the potential region starting from the onset of HER up to 1.0 V, although processes taking place are not relevant for HER which occurs at lower potentials. Cyclic voltammograms of pure Au(111) surface and of Rh/Au(111) nanostructures are presented in Fig. 2. Due to the presence of Rh nanoislands on Au(111) substrate, currents associated with the reconstruction of Au(111) surface and with the lifting of the reconstruction as well as butterfly peaks at 0.8 V characteristic for the ordered sulfate adlayers on the Au(111) surface [14] are suppressed. There are no peaks associated to the hydrogen adsorption on obtained Rh/Au(111) nanostructures as in the case of Rh(111) single crystal [15] and pseudomorphic Rh overlayer on Au(111) [9], where sulfate adsorption occurs in a narrow potential region and competes with hydrogen adsorption. Therefore, the absence of hydrogen adsorption peaks is indicative of an island growth and can be attributed to the stronger electronic effect of Au(111) substrate. Sulfate adsorption on Rh/Au(111) surfaces is associated with reversible peaks in the potential region from approx. 0.3 V to 0.7 V, which are slightly shifted compared to pure Au(111). Current associated to sulfate adsorption is almost independent on Rh coverage. This indicates that Rh islands are both geometrically and energetically suitable for sulfate adsorption like Au(111) surface sites, meaning that Rh islands are mainly (111) oriented and that the electronic effect by the gold substrate is strong enough. This is in agreement with the results obtained for sulfate adsorption on Pt [12] and Pd [3] nanoislands, spontaneously deposited on Au(111).

Oxidation of the deposited Rh islands occurs at higher potentials simultaneously with sulfate desorption. On the reverse sweep, Rh oxide reduction overlaps with sulfate adsorption and proceeds up to the beginning of HER, indicating that a partial cationic nature of the deposited Rh islands is preserved even at lower potentials.

3.3. Hydrogen evolution on Rh/Au(111)

Polarization curves for hydrogen evolution on different Rh/Au(111) nanostructures and on pure Au(111) in 0.5 M H_2SO_4 solution are presented in Fig. 3. For comparison, polarization curves for HER for

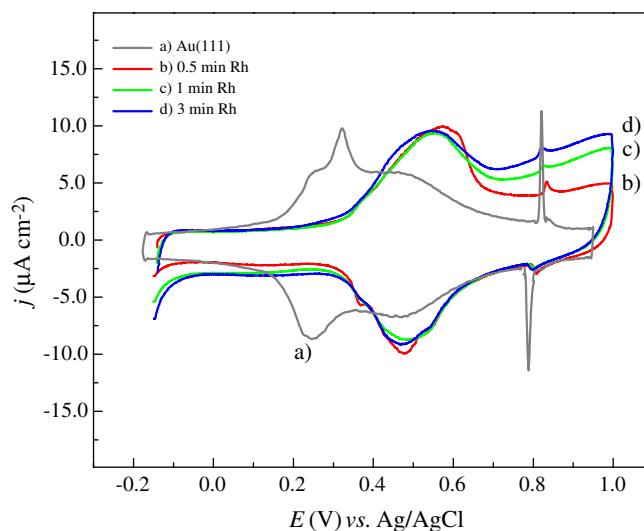


Fig. 2. Cyclic voltammetry of Rh/Au(111) surfaces obtained by spontaneous deposition of Rh for various deposition times. Curves are recorded in 0.5 M H_2SO_4 with the scan rate of 50 mV s^{-1} .

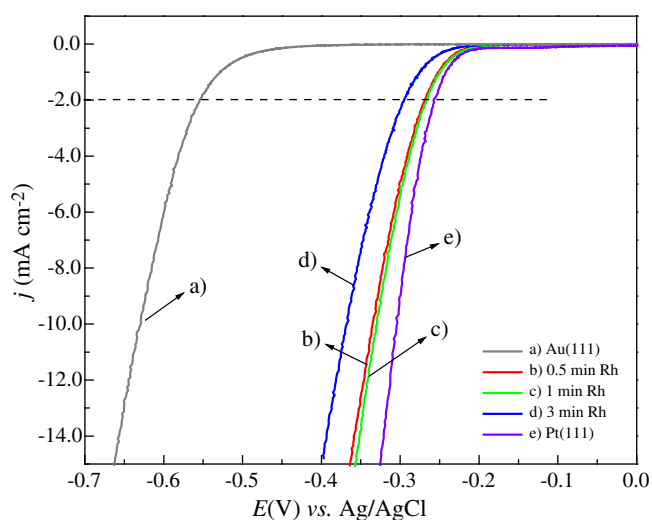


Fig. 3. Polarization curves of hydrogen evolution on Au(111), Rh/Au(111) nanostructures and on Pt(111). Curves are recorded in 0.5 M H₂SO₄ solution with the scan rate of 10 mV s⁻¹.

Pt(111) obtained in the same solution are also presented. While on pure Au(111) hydrogen evolution occurs at rather high overpotentials, it is significantly catalyzed by the presence of Rh nanoislands with the coverage up to 50%, obtained after 0.5 and 1 min Rh deposition (see Fig. 1a and b). For a higher Rh coverage of 90%, obtained after 3 min deposition (see Fig. 1c and d), the catalytic activity of such Rh/Au(111) surface for HER is lower and decreases even more with a further increase of the amount of the deposited Rh during prolonged immersion (not shown).

For the same current density of -2.0 mA cm^{-2} , the potential for HER for the most active Rh/Au(111) surfaces obtained for 0.5 and 1 min Rh deposition, is shifted positively for 285 mV with respect to the pure Au(111) surface. It is worth noting that this catalytic activity is for 80 mV higher than one obtained for Pd/Au(111) surface for the same coverage of approx. 50% [3], and only 10 mV short of the Pt(111) activity. For surfaces obtained for 3 min Rh deposition, the activity for HER is 25 mV lower with respect to the most active Rh/Au(111) surfaces.

Tafel slopes for HER on Rh/Au(111) nanostructures as well as for HER on pure Au(111) and Pt(111) electrodes are given in Fig. 4. For Au(111) electrode, one well-defined Tafel slope of $b_1 = -110 \text{ mV dec}^{-1}$ could be assigned to Volmer–Heyrovsky mechanism [3], while for Pt(111) due to Tafel slope of $b_2 = -60 \text{ mV dec}^{-1}$, the mechanism could be either Volmer–Heyrovsky or Volmer–Tafel under Temkin conditions [16]. Similar Tafel slopes of $-55 \pm 5 \text{ mV dec}^{-1}$ are obtained on different Rh/Au(111) nanostructures, which can be explained by the same two mechanisms suggested for HER on Pt(111). However, based on DFT calculations [6], the energy of activation for both Volmer and Tafel reactions is very low. Hence, it is reasonable to suggest that Volmer–Tafel mechanism is more likely. On the other hand, for this mechanism, Tafel slope of $\sim -60 \text{ mV dec}^{-1}$ could be only obtained if Tafel (recombination step) is a rate determining under Temkin adsorption conditions, due to the strong lateral interactions between adsorbed intermediates. High activity of Rh/Au(111) nanostructures for HER could be ascribed to an upshift of the d-band center which occurs due to the strain caused by a particularly large lattice mismatch (lattice constant of Rh is 0.269 nm, and 0.288 nm of the Au(111)) as discussed in Refs. [6,7]. The highest activity obtained for 50% Rh coverage, where the deposit consists of small Rh islands suggests that in this case the electronic effect is more pronounced than in the case of larger Rh islands (e.g. for 3 min Rh deposition).

It is worth noting that the experimental confirmation of the theoretically predicted high activity of Rh/Au(111) system for HER [6,7],

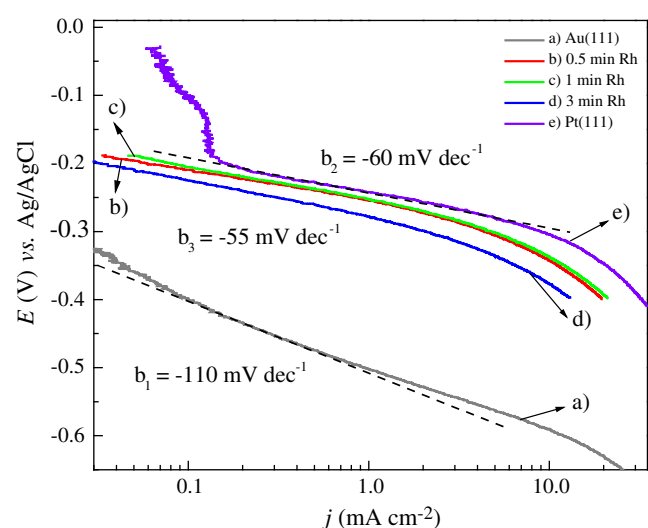


Fig. 4. Tafel plots for HER on Au(111), Rh/Au(111) and Pt(111) surfaces in 0.5 M H₂SO₄ solution obtained from the data from Fig. 3.

points out that the experiment can be successfully guided by the theoretical prediction, and emphasizes a necessity to make a stronger link between theory and experiment in modern electrocatalysis.

4. Conclusions

Rh/Au(111) nanostructures obtained by the spontaneous deposition of Rh nanoislands on the Au(111) at submonolayer coverage have shown very pronounced catalytic activity toward HER in acid solution. This activity exceeds that of Pd/Au(111) and approaches that of Pt(111), which is explained by the stronger electronic effect of the Au substrate on Rh islands. Experimental findings are in excellent agreement with theoretically given predictions.

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