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Short Communication

Gold electrodes with rough surfaces. The Golden Hedgehog Project

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ABSTRACT

A simple and technologically relevant way for Au surface roughening based on two physical processes is described: subjecting Au surface to mercury vapors and forming gold amalgamate followed by a thermal decomposition of the amalgamate under vacuum. All mercury is removed yielding the Au surface with numerous spine-like protrusions 2–4 μm high and separated from each other by a few μm. A special tester is prepared with two working Au electrodes and two counter electrodes of which one pair of WE + CE underwent amalgamate roughening (the other pair remained unchanged). Electrochemical measurements show that the tester with the roughened Au electrode has a surface area larger than the tester with untreated Au electrode by 20–160% depending on the method. Advantages of this process in comparison to other methods for Au roughening are briefly discussed.

1. Introduction

Recently an increased demand has been observed for roughened, porous gold films. These porous gold structures have multiple applications in catalysis, medicine and as sensors [1–8]. Biocompatibility, high conductivity and chemical resistance make these Au films a perfect platform for building functional biosensors. Gold acts here as a transmitter that translates the biochemical signal to a measurable physical property. Also gold may act as platform for binding reactive centers in many different contexts (cells, proteins, antigens). The fact that Au film is roughened makes the real 3D surface larger than its geometrical area, which allows for higher sensitivity, better precision, smaller error and miniaturization of devices using such surfaces. Other applications for roughened gold films involve photovoltaics [9], where higher and roughened surface area means more effective light trapping and therefore higher efficiency of solar cells. Yet another application for roughened gold film is SERS (Surface Enhanced Raman Spectroscopy) [10–12]. A number of ingenious and often very interesting methods for gold roughening were developed, usually based on chemical reactions of selective Au etching or reduction of Au salt precursors [6–8,13]. Below, we describe a new method for roughening gold electrodes that uses physical methods that are well known in semiconductor industry – operations involving vacuum and high temperatures. Recently transformation of continuous gold film into isolated amalgamate islands of nanometer scale has been demonstrated [14]. In our method Au thin films are treated in vacuum with mercury vapors resulting in formation of a gold amalgamate. During the process, the shiny gold surface turns to silver metallic. The amalgamate is then thermally decomposed at high temperature in vacuum which results in a complete removal of mercury and all Au is recovered in the form of rough Au surface. Roughened Au electrode surface with spiny-like structures 2–4 μm high that are separated by 2–4 μm from each other resembles “hedgehog” which prompted us to name this research “The Golden Hedgehog Project”. There is no need to use additional chemicals in contrast to other processes for seeding and growth of Au clusters, (nanorods). The entire process is controlled by technological parameters i.e. the pressure; the temperature and the time.

2. Experimental

Fig. 1A shows the specially designed sensor with two Au working electrodes and two Au counter electrodes. The sensor enabled direct comparisons between untreated and roughened Au working electrodes (WE) in the cyclic voltammetry (CV) experiments. In the first CV run the unmodified Au WE was used while in the second run the roughened Au WE was used. Both experiments used the same reference electrode. Testers were deposited onto 1″ × 1″ glass slides in accordance with the procedure presented in Fig. 1B.

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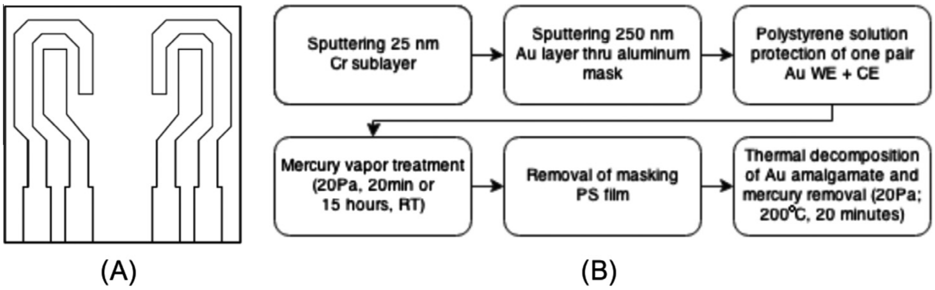

Fig. 1. (A) Tester with two Au working and two counter electrodes and (B) block diagram for testers production.

2.1. Cyclic voltammetry (CV)

Cyclic voltammetry experiments were performed using a potentiostat (CH Instruments 1040A for measurements with redox probe and Bio-Logic VMP for direct gold oxidation–reduction) with a standard three-electrode system to estimate the real Au WE surface changes after amalgamation/roughening step. The electrolyte solution consisted of (a) 0.1 M KCl; 0.5 mM $K_4[Fe(CN)_6]$; 0.5 mM $K_3[Fe(CN)_6]$ or (b) 0.1 M PBS (phosphate buffer solution) pH = 7.4 for direct gold oxidation–reduction. Reference electrode (RE) was an Ag/AgCl/1 M KCl electrode.

2.2. Atomic Force Microscope (AFM) studies

Surfaces of two WE Au electrodes (unmodified and roughened) were compared using AFM Park Systems XE-120 operating in a contact mode. At least two tips (PPP-CONTSCR, Nanosensors) for each sample were used to ensure reproducibility. All scans were performed under ambient conditions. Several images at different scan sizes and various places for each sample were taken to gain better knowledge of the variations of local structures. For all images we started with the same values of scan parameters, however in each case, final optimizations were performed.

2.3. Raman spectroscopy

Rhodamine B was deposited onto unmodified and roughened electrodes for Raman spectroscopy. Measurement of Rhodamine B adsorbed on the surface was conducted using Nicolet Almega XR spectrometer in air. For this purpose 523 nm laser was used. Deposition of Rhodamine B was done through following procedure: first, testers were cleaned with water, acetone and isopropanol. Then they were submerged into 0.01 M Rhodamine B solution in ethanol for 24 h. After that testers were rinsed thoroughly in ethanol three times and dried in air.

3. Results and discussion

3.1. AFM measurements

AFM images of Au electrodes unmodified and roughened (amalgamated) for 20 min or 15 h are presented in Figs. 2 and 3 respectively. Note: Figs. 2A and 3A are results coming from different samples.

From AFM measurements it is possible to calculate the parameters which characterize the rough surface [15,16]. The following surface parameters are taken into account: (i) the root-mean-square (RMS) surface roughness defined as:

$$\sigma^2 = \langle (h(x,y) - \langle h(x,y) \rangle)^2 \rangle,$$

where $h(x,y)$ is the height of the surface element at point (x,y) and $\langle h(x,y) \rangle$ denotes the mean height of surface features and (ii) the roughness factor which is the surface to projected area ratio. In Figs. 2 and 3 AFM images and surfaces profiles from randomly selected $10 \times 10\ \mu m^2$ areas of investigated samples are presented. For each surface several local profiles of various places of the sample were taken. The average RMS surface roughness is equal to 2.80 nm and the average roughness factor is equal to 1.0153 for the untreated Au surface. After amalgamation process and thermal vacuum amalgamate decomposition a significant increase of the surface parameters was observed. The average RMS surface roughness increased from 57.31 nm (20 min of amalgamation) up to 186.76 nm (15 h of amalgamation). The same trend was observed for the average roughness factor values: from 1.0620 (20 min of amalgamation) up to 1.1237 (15 h of amalgamation). It can be clearly seen that amalgamation forms a highly roughened gold surface. Gold "spines" formed after the decomposition of the amalgamate and the longer contact of Au with mercury vapors yielded the "spines" that were thicker, with diameter of about 4 μm compared to the thinner "spines" of about 1–2 μm observed with shorter amalgamation time. There are three important features of such method for Au surface roughening. Firstly there is no loss of gold, in contrast to other etching procedures where always a part of the gold electrode is dissolved. Secondly, no mercury traces were detectable by XPS measurements on the roughened Au electrode surface, therefore purity of the gold surface was preserved [13]. Thirdly, when the Au electrode layer was at least 200 nm thick, the roughening procedure yielded the film which was still electroconductive and it should be noted that there were no separated gold islands but a "spiny" Au continuous layer [17].

3.2. CV results for measurements with redox probe

Cyclic voltammetry experiments for unmodified and roughened Au WE electrodes were performed using three different scan speeds 20; 50 and 100 mV/s. Sample amalgamated for 15 h was used in this measurement. The starting potential was −0.6 V and the end potential was 0.9 V. Results are presented in Fig. 4. Data for sample amalgamated for 20 min showed a similar character but about two times smaller than the effects observed for the sample amalgamated for 15 h.

All scans showed the same feature – the roughened Au WE showed a bigger active surface. This made both the oxidation and the reduction peaks higher than the same peaks observed for unmodified Au WE. Decreased values in separation between oxidation/reduction peaks were also observed, indicating a more reversible process for roughened Au electrodes. This might be coming from higher surface activity of roughened gold that might promote easier oxidation and reduction of redox probe. Higher surface activity can have a source in a high disorder or internal stress in roughened Au structure that is a result of rapid mercury evaporation from amalgamate. Peak currents grow linearly with square root of scan speed which suggests that diffusion is only limiting factor in redox reaction. According to Randles–Sevcik equation