Preparation of nano- and microstructured gold surfaces by application of a square wave potential regime

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Gold nanometallic structures have been prepared by application of square wave potential regime to a platinum electrode in a $1.0\text{x}10^{-3}$ M $HAuCl_4$ + 0.5 M H_2SO_4 solution. Formation of gold particles onto the platinum surface has been followed by cyclic voltammetry, energy-dispersive X-ray spectroscopy, and scanning electron microscopy. The results indicate that the size, shape, uniformity of distribution of the particles are affected by the selected parameters of the applied square wave potential regime. Parameters of the square wave include the frequency, the lower and the upper limits of the square wave and the time of application of the square wave potential regime. The concentration of $HAuCl_4$ in the solution is another important factor. The results of the present work indicated that the 100 Hz frequency is the optimal frequency for obtaining gold nanoparticles on platinum surface. Deposition time has been also found to play a critical role in affecting the size, shape and homogeneity of gold nanostructures at the surface. The surface coverage with nanoparticles as calculated from the decrease in the charge of hydrogen adsorption/desorption peaks is found to be directly proportional to the time of application of the square wave. Testing the nanostructured gold/Pt electrode for oxidation of formic acid shows its higher catalytic activity than that of platinum and gold plain electrodes.

Keywords: nanostructured electrodes, gold electrodes, square wave, preparation of electrodes.

УДК 621.35

INTRODUCTION

The search for new electrodes with enhanced electrocatalytic properties or electrodes which show specificity or enhanced electroanalytical selectivity has been the goal of electrochemists for decades [1, 2]. Modified electrodes, faceted electrodes, adatom electrodes and recently nanoelectrodes have been the scope of numerous publications with a variable degree of success in pursuing the objectives of enhanced reactivity and/or selectivity [3–6]. Nanostructures and nanoparticles, the state-of-the art technology appeared as providing a new dimension of materials of special properties [7]. These structures have received considerable attention because of their unusual and interesting electrocatalytic properties [8, 9] which also allowed them to be used as sensors in many analytical applications [10]. Preparation of nanoparticles and nanostructures by chemical and electrochemical methods has been described elsewere [11]. Among those methods is the electrodeposition or the electrochemical approach to preparation of nanoparticles and nanostructured surfaces.

The electrochemical approach towards preparation of nanostructures and nanoparticles provides advantages in terms of simplicity, reversibility of modified surfaces and the high control of nucleation and particle growth during preparation through the control of electrochemical experimental parameters [12, 13].

The present work offers a new method for electrochemical preparation of metallic nanostructures by application of a square wave potential regime. Application of a square wave potential regime to the electrode induces episodes of deposition and/or dissolution at the electrode surface depending on the selected square wave parameters [14]. The alternation of these episodes with the optimized parameters of the square wave, that is, high and low values, and the frequency of the square wave is supposed to control the relative rates of the particle growth and the nucleation mechanism. Upon control of the other experimental parameters, this approach may provide an opportunity to control the particle size, distribution, crystallography, composition, and consequently the reactivity of the nanostructured surfaces with an ultimate goal of preparation of highly catalytic nanostructured surfaces.

EXPERIMENTAL

Materials, instruments, cells and electrodes

A potentiostat (273 A, Princeton Applied Research) interfaced to a computer through a GPIB interface along with Echem® software was used for electronic control and data acquisition. A conventional H-shape electrochemical cell equipped with a multiple inlet system for admission of supporting electrolyte, purging and covering the solution with oxygen-free nitrogen was used. The reference electrode was an Ag/AgCl/[Cl^-] = 1.0 M, and all the potentials reported in the present paper are referenced against this electrode. The working electrode was a 1.0 mm-diameter electrode or a platinum foil attached to a platinum wire (99.99% pure, Johnson Matthy). The immersed part of the wire was curved in order to provide a mark for consistent surface area.

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All reagents used were highly pure certified analytical reagent (A.R.) chemicals and used as received from the suppliers without further purification. The working and the auxiliary electrodes were made of platinum (Johnson Matthy, 99.99% purity). The purging nitrogen was supplied by the National Gas Company and coupled with Oxisorb® cartridge (Suplico) to remove traces of oxygen. All solutions were made from the above mentioned reagents dissolved in triply distilled water where the second distillation was carried out from a basic potassium permanganate solution to get rid of any traces of organic impurities.

The deposition cell

Polarographic 303A cell was used for the electrodeposition of gold nanostructures. The cell was modified by bypassing the electronic circuitry of the 303 plarographic stand and using the three electrode cell system for the deposition process with Ag/AgCl, $[Cl^-] = 1.0$ M reference electrode. The 0.5 M H_2SO_4 +1.0 $x10^{-3}$ M $AuCl_4^-$ solution was stirred during the deposition time and purged with oxygen-free nitrogen gas.

Procedures

Initially the electrode was cleaned by immersion in a freshly prepared chromic acid solution for five minutes. The electrode was conditioned by cycling the potential between the hydrogen evolution and oxygen evolution limits (-0.25 and 1.35 V) until the regular voltammogram of polycrystalline platinum was produced (Fig. 1).

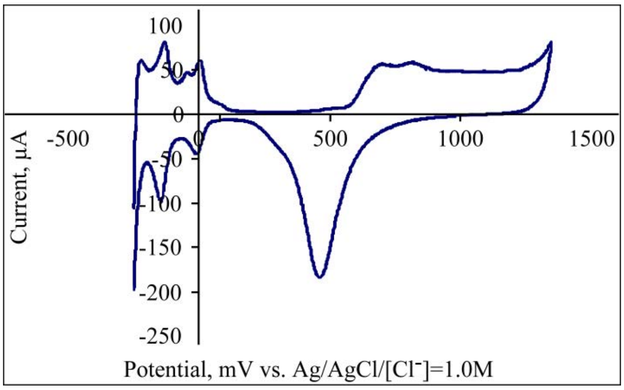

Fig. 1. Cyclic voltammogram of polycrystalline Pt electrode in 0.5 M H_2SO_4, $dE/dt = 100$ mV/s.

The square wave with the preset amplitude and frequency was generated by a function generator Simpson, A 240. The square wave was fed to the potentiostat at the external input. The desired lower and higher limits of the potential regime were obtained by adjusting the applied electrode potential from the potentiostat. During deposition the gold solution was stirred using a magnetic stirrer. The duration of applying the square wave potential regime was varied and the obtained structures were viewed by the scanning electron microscope (SEM) Inspect^{TM} F50, FEI, to determine the optimal time for deposition in terms of distribution, uniformity, size and shape of the produced nanostructures.

The frequency of the square wave was also varied between 10 and 1 kHz to explore the influence of frequency on the formed particles. The gold nanoparticles on platinum substrate electrode were investigated after deposition by cyclic voltammetry and SEM. Formic acid with a concentration of $1.0x10^{-2}$ M in 0.5 M H_2SO_4 was used to test the catalytic behavior of the nanostructure surfaces. All of the experiments were performed at ambient temperatures.

RESULTS

The effect of square wave frequency

Figure 2 shows gold nanoparticles developed atop of a platinum surface by application of a square wave potential regime between -0.300 and 0.1 V for 2.00 min at different frequencies. The SEM micrographs were analyzed in terms of the particle size, its shape and homogeneity of distribution of the particles. These micrographs show that at low frequencies, 100 Hz or lower, gold nanostructures have better distribution on the platinum surface. The nanostructures prepared by application of a 500 Hz or higher frequencies were found to have a high degree of aggregation and to be deposited in islands. A rough estimate of the average particle diameter for the particles deposited by application of 100 Hz square wave for a period of 2 min. is ranging from 8 to 10 nm in contrast to other frequencies where it ranged from 10 to 15 nm. The surface coverage assessed by the degree of closeness of the particles corroborates the conclusion based on voltammetric measurements that 100 Hz is the optimal frequency for electrodeposition of gold nanoparticles.

Figure 3 shows an example of the EDX spectrum for one of the deposited particles. The EDX spectrum shows platinum, gold and oxygen as the major peaks. This positively proves the identity of the deposited gold nanoparticles on a platinum substrate.

The above-mentioned conclusions about the effect of frequency on the deposited nanoparticles are confirmed by the voltammetric data. Figure 4 shows an example of a voltammogram of a nanostructured electrode produced by application of a 1 kHz-square wave potential regime. The voltammetric features of the well-known polycrystalline gold electrode, i.e., oxygen adsorption and desorption peaks, are clearly manifested on the voltammogram. The voltammetric features of platinum, hydrogen adsorption/desorption and oxygen adsorption/desorption peaks are also obvious on the voltammogram. In fact, the voltammogram of the gold nanoparticles deposited on the Pt substrate electrode is a hybrid between the voltammograms of polycrystalline platinum and those of polycrystalline gold electrodes. Compared with voltammetric features of the unmodified platinum electrode, the modified electrode exhibits severely reduced hydrogen adsorption and desorption peaks due to the decrease in the platinum available surface area available for hydrogen adsorption.

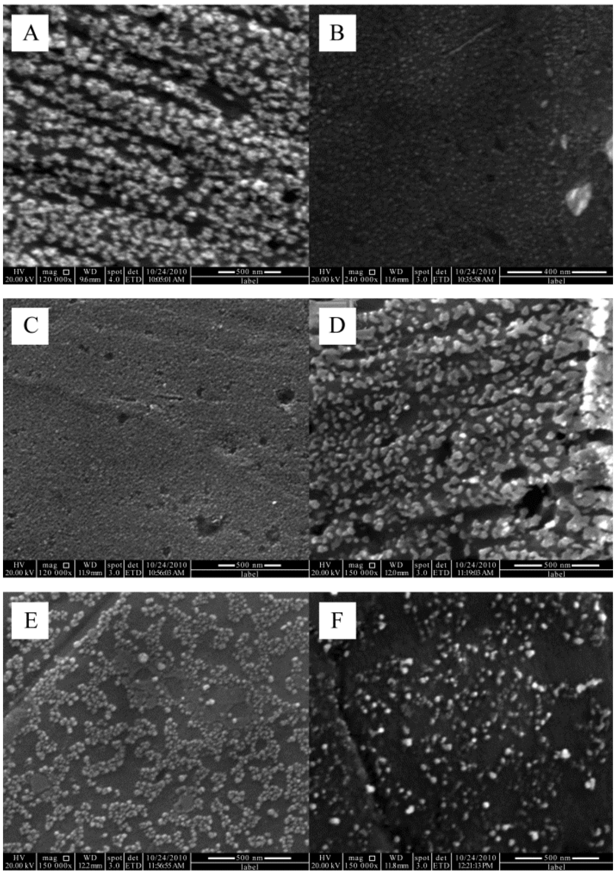

Fig. 2. SEM micrographs of gold nanoparticles deposited on platinum substrate. Deposition was carried out by application of A: 10 Hz, B: 50 Hz, C: 100 Hz, D = 500 Hz, E: 750 Hz and F: 1 kHz square wave potential regime between the limits, E_l = -0.3 and E_u = 0.1 V. Deposition time = 2 min.

Surface coverage with gold nanoparticles was quantified from the degree of suppression of hydrogen adsorption and desorption as referenced to the unmodified platinum electrode. The coverage with gold nanoparticles was calculated according to the following equation:

$$\theta = 1 - \frac{H_{modified\ electrode}}{H_{bare\ electrode}},$$

where $H_{modified}$ is the charge underneath the hydrogen adsorption or desorption peak for the platinum electrode modified with gold nanoparticles and H_{bare} is the charge underneath the hydrogen adsorption or desorption peak for the plain platinum electrode. The coverage with gold nanoparticles as a function of the applied square wave frequency is given in the Table. Similarly to our conclusions based on the SEM micrographs, the data given in the Table show that 100 Hz is the optimal frequency for the applied square wave. These results are not unexpected. That is, each cycle of the square wave can be considered as a double potential step experiment. Thus, the train of pulses constituting the square wave can be envisaged as a repetitive double-potential step experiment. The duration of time (τ) spent at the lower limit (E_l = -0.30 V) affects the relative rates of the competing mechanisms; nucleation and particle growth and consequently the size of the formed particles.

Table. Platinum surface coverage with gold nanostructures on platinum substrate prepared by application of a square wave at diffrenet frequencies for 2 min. Solution: 1.0 M H_2SO_4 + $1x10^{-3}$ M $HAuCl_4$. Square wave limits; E_l = -0.30 V and E_h = 0.10 V

Square wave frequency	Coverage with gold
10 Hz	0.89
50 Hz	0.83
100 Hz	0.98
500 Hz	0.84
750 Hz	0.79
1 kHz	0.72

The effect of deposition time

Application of a square wave between -0.3 and 0.1 V with a 100 Hz frequency at different deposition times was found to affect the uniformity of distribution; size and shape of the deposited particles (Fig. 5). At longer deposition times, 10 and 15 minutes, three-dimensional microstructures tend to form on the platinum surface. These three-dimensional structures or formations only cover a fraction of the platinum surface as indicated by the SEM micrographs and i-E traces. At lower deposition times, smaller particles with better distribution on the surface were formed. The optimal deposition time which comprises the particle size and uniformity of distribution on the surface was 2 min.

Electrocatalytic activity of naostructured gold/platinum electrode

The electrooxidation of formic acid has been studied extensively due to its importance in understanding the mechanism of electrocatalysis of small organic molecules [15].

Figure 6 shows the voltammogram of gold nanoparticles deposited on a platinum substrate recorded in a 1.0 $x10^{-3}$ M HCOOH + 0.5 M H_2SO_4 solution. In the same figure, the voltammograms recorded under the same experimental conditions, for both gold and platinum electrodes are displayed. Upon investigation of the three voltammograms, the voltammetric features for oxidation of formic acid at the gold nanostructured/platinum electrode are simi-

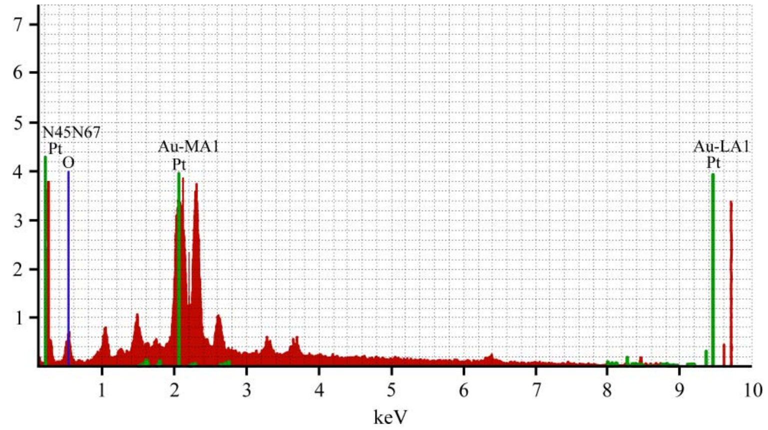

Fig. 3. EDX-ray spectrum for a gold nanoparticle deposited on platinum substrate. Deposition was carried out by application of a 100Hz square wave between the limits -0.3 V and 0.1 V. Deposition time = 2 min.

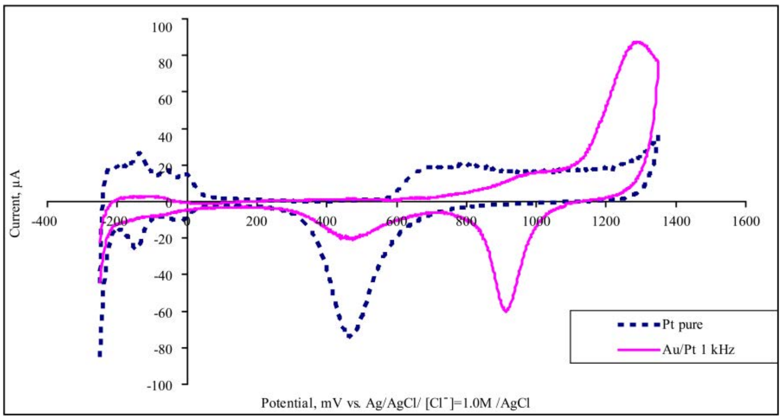

Fig. 4. Cyclic voltammogram of Au nanoparticles deposited on a platinum substrate prepared using 1 kHz-square wave potential regime. Experimental parameters: solution: 0.5 M H_2SO_4, dE/dt = 100 mV/s, deposition time = 2 min.

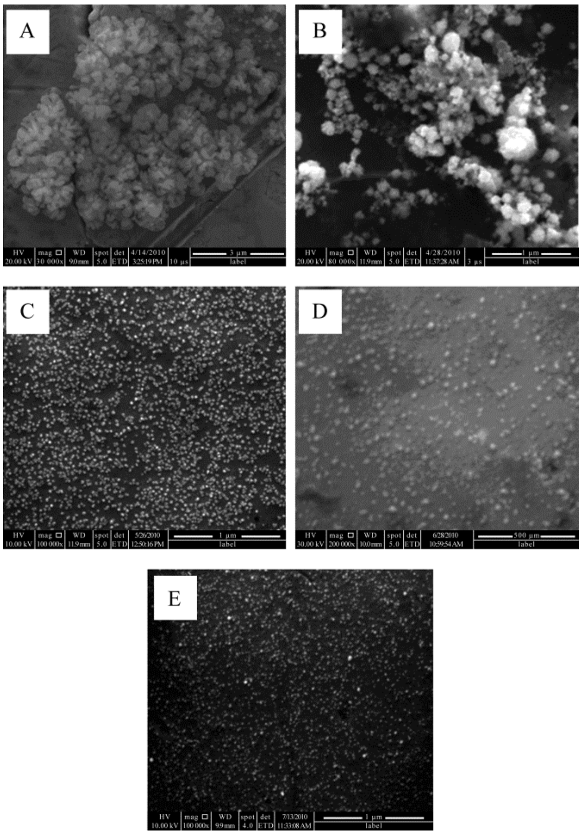

Fig. 5. SEM micrographs of gold nanoparticles deposited on platinum substrate. Deposition was carried out by application of 100 Hz quare wave potential regime between the limits, E_l = -0.30 V, E_u = 0.1 V at deposition times of A = 15, B = 10, C = 5, D = 2 and E = 0.5 min.

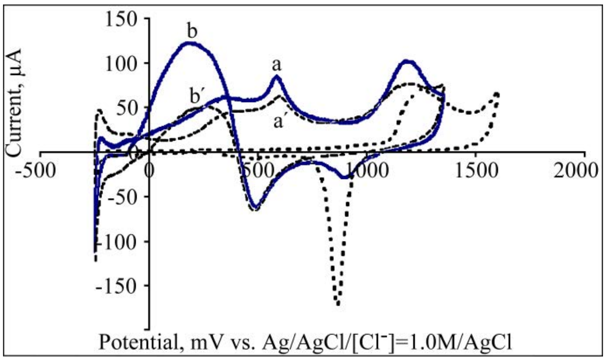

Fig. 6. Cyclic voltammogram of formic acid oxidation on Au/Pt 100 Hz modified electrode (the solid line). (Dashed line is the voltammogram recorded at Pt electrode and the dotted line is the voltammogram at Au electrode). Experimental parameters: solution: $1x10^{-2}$ M formic acid in 0.5 M H_2SO_4, dE/dt = 100 mV/s.

lar to the voltammetric features of oxidation of formic acid at platinum electrode. This result is not unexpected since platinum electrode, in general, is more active in electrooxidation of formic acid than gold electrodes [16]. There are, however, some differences between the voltammetric features of oxidation of formic acid at the nanostructured gold /platinum electrode and the bare platinum electrode. The nanogold/Pt electrode displays greater similarity to the Pt bare electrode than to the gold one. Higher activity of the modified electrode is manifested through three observations. The first observation is the appearance of the first formic acid oxidation peak (Fig. 6: peak a) at 0.567 V compared to 0.586 V (Fig. 6: peak a'). The second observation is the appearance of the formic acid oxidation peak on the negative-going scan where it appears at 0.173 mV at the modified electrode compared to 0.250 V at the bare platinum electrode. The third observation is a much higher peak current observed for the formic acid oxidation on the negative going scan (Fig. 6: peaks a and a'). The shift in peak positions towards more negative potentials indicates an electrocatalytic effects imparted by gold nanoparticles. The increase of the area for oxidation peak of formic acid is also a manifestation of an electrocatalysis in the electrooxidation of formic acid and is simply attributed to a significant expansion of the surface area provided by gold nanoparticles. Though the platinum electrode surface is mostly covered by gold nanoparticles, the voltammetric features for the oxidation of formic acid are very similar to the voltammetric features of platinum. This observation can be explained in the following way: the electronic states of the gold-Pt surface are modified and merge together rendering the surface behaves like a gold-platinum alloy rather than gold or platinum localized spots with separate electronic surface states.

CONCLUSIONS

Application of the square wave potential regime at a platinum electrode in a solution containing $HAuCl_4$ solution developed gold nanostructures on the surface of the platinum electrode. SEM micrographs and cyclic voltammograms allow us to conclude that the size, shape, distribution and homogeneity of the formed structures depend on the deposition time and the frequency of the applied regime. The optimal deposition time was found to be 2 min. and the optimum frequency 100 Hz. These parameters have been chosen based on the criteria of distribution, homogeneity and uniformity of the deposited nanostructures.

The electroactivity of the modified electrode was tested towards the oxidation of formic acid. The results showed that the modified electrode has excellent activity compared to that of plain gold and platinum electrodes.

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Реферат

Золотые нанометаллические структуры были получены путем использования режима квадратно-волнового изменения потенциала применительно к платиновому электроду в растворе H_2SO_4 1,0x10^{-3} M $HAuCl_4$ + 0,5 M. Формирование золотых частиц на платиновой поверхности было исследовано затем путем циклической вольтамперометрии, EDX-спектроскопии и SEM. Результаты исследования показывают, что размер, форма и однородность распределения частиц зависят от выбранных параметров приложенного потенциала квадратной формы. Параметры волны включают в себя частоту, нижний и верхний пределы изменения потенциала и время его применения. Концентрация $HAuCl_4$ в растворе является еще одним фактором. Результаты данной работы показывают, что частота 100 Hz является оптимальной для получения золотых наночастиц на платиновой поверхности. Время осаждения также оказывало влияние на размер, форму и однородность золотых наноструктур на поверхности. С учетом уменьшения заряда пиков адсорбции/десорбции водорода было рассчитано, что покрытие поверхности наночастицами прямо пропорционально времени прямоугольного импульса. Тестирование наноструктурного электрода золото/Pt на предмет окисления муравьиной кислотой показало более высокую активность по сравнению с платиновым и чисто золотым электродами.

Ключевые слова: наноструктурированные электроды, золотые электроды, квадратноволновой потенциал, изготовление электродов.