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Decoration of nanoporous stainless steel with nanostructured gold via galvanic replacement reaction and its application for electrochemical determination of dopamine

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ABSTRACT

A stainless steel substrate with highly ordered self-organized nanopores was decorated with gold nanostructures (Au/NPSS) for use in electrochemical biosensors. The nanopores were formed on stainless steel surface using anodization process, filled with Cu using pulsed electrodeposition and followed by galvanic replacement of Cu with gold. The characteristics of the electrode and its potential application for electrochemical determination of dopamine (DA) were investigated using scanning electron microscopy, energy-dispersive X-ray spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy. The results indicated that compared to a smooth gold electrode, the nanostructured gold film formed on the NPSS has a great active surface area and displays a higher peak current for DA oxidation. Cyclic voltammetric determination of DA exhibited two wide linear ranges of 3.0–8.0 and 8.0–2000 μM with a detection limit of 0.07 μM ($3S_b/m$). Moreover, two lines in the range of 1.0–80.0 μM of DA with a limit of detection of 0.02 μM ($3S_b/m$) were obtained using differential pulse voltammetry. Au/NPSS exhibited good repeatability and reproducibility, long-term stability and acceptable selectivity. This work opens up new prospects for the fabrication of inexpensive noble metal-based catalysts supported on NPSS, which have a potential application in biosensors.

1. Introduction

Stainless steel (SS) possess novel characteristics such as low-cost, high mechanical strength and corrosion resistance, biocompatibility, good electrical conductivity and commercial availability, which have made it an attractive alloy material for the fabrication of many clinical and biomedical tools and devices [1,2]. Moreover, it has been proved that the chemically modified SS substrate as an inexpensive and disposable electrode material has a great potential application in biosensors, especially in needle-type biosensors [3–6]. Accordingly, there is a tremendous interest in our research group to design and fabricate SS medical tools (such as vascular stents, injecting needles, guide wires and orthopedic implants) which can also be used for in vivo determination of biomolecules or drugs in tissues or biological fluids. To achieve this goal, the modification of SS surface with biocompatible materials or metals which are able to monitor biomolecules sensitively and selectively is necessary. Gold nanostructures, due to their high active surface area, chemical stability, excellent electrical conductivity, superior catalytic activity and biocompatibility, have been widely used as a support for catalysts or/and bio-molecules in many high-performance electrochemical biosensors [7–9]. However, the weak adhesion of gold to SS is a major challenge because the catalyst–support interaction is a key factor which influences the electrochemical activity and stability of heterogeneous catalysts. Compared with smooth SS surface, the adhesion of coatings on nanostructured surface is better [10,11]. Electrochemical anodization process has extensively been used to form highly ordered self-organized nanopores on SS surfaces [12,13]. However, a few papers have reported the use of the anodized SS as the substrate in sensors and biosensors.

Electrodeposition of metallic atoms into nanopores of a hard nanoporous template is a promising powerful and inexpensive bottom-up approach to the fabrication of arrays of nanostructured materials. In this technique, the size, shape and density of nanostructures are easily tuned by controlling the electrodeposition and template parameters [14,15]. Moreover, there is no need to surfactants, oxidants, reducing or stabilizing reagents which may contaminate the nanostructured materials and reduce their performance.

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Galvanic replacement is another simple, low-cost, well-established and non-hazardous chemical way developed to fabricate metal (especially noble metal) nanostructures on a substrate. GR occurs when a less-noble metal substrate is exposed to a solution containing more noble metal ion precursors. Since the difference between the equilibrium potential of two metals is positive, a spontaneous electrochemical reaction takes place in the interface of the electrode, which leads to spontaneous deposition of the more noble metal on the electrode surface and dissolution of the less noble component [16,17]. The major advantage of this method is the ability of loading low amount of metals with high active surface area on the surface, which is very important in the case of expensive and rare noble metals such as Pt, Pd and Au. The electrocatalytic behavior of some metallic or alloyed gold nanostructures prepared via GR process have been investigated in some electrochemical biosensors [18–20].

In our previous work [11], it was shown that the nanoporous SS can act as a hard template which its pores are easily filled with Cu through pulsed electodeposition. It was also shown that the formed Cu nanostructures on the SS surface, without being removed from the SS pores, as the sacrificial metal can be replaced with Pd for use in alkaline fuel cells. It was demonstrated that the presence of the nanopores on the SS surface plays an important role in long-term stability of the catalyst film. In this study, we modified this method to fabricate nanoporous SS-supported nanostructured gold which has a potential application in electrochemical biosensors as an inexpensive and disposable substrate. Therefore, the loading of gold nanostructures on the nanoporous SS was performed through GR reaction using Cu sacrificial metal electrodeposited into nanopores of SS. The morphology and electrochemical behaviors of the prepared electrode (Au/NPSS) were characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). In comparison with a poly-crystalline flat gold electrode, Au/NPSS displayed higher active surface area. Finally, the applicability of Au/NPSS in electrochemical biosensors was investigated by electrochemical determination of dopamine (DA).

DA, (3,4-dihydroxyphenyl)ethylamine, is one of the most important catecholamine neurotransmitters, which plays an essential role in the function of the mammalian central nervous, renal, hormonal and cardiovascular systems [21,22]. Parkinsonism, schizophrenia, Alzheimer's and Huntinton's disease, drug addiction and HIV infection are serious diseases resulted from either low concentration or abnormal metabolisms of DA [23–25]. Therefore, it is necessary to accurately determine DA in pharmaceutical and biological samples. Although so far various analytical methods, such as high performance liquid chromatography [26], chemiluminescence [27] and surface plasmonic detection [28], have been developed for DA determination, electrochemical techniques based on a chemically modified electrode are usually preferred because of their simplicity, low-cost, rapidity and high sensitivity.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and obtained from Merck. A 10 mM stock dopamine solution was freshly prepared by the dissolution of dopamine hydrochloride purchased from Merck (Darmstadt, Germany) in an appropriate volume of double distilled water. 0.10 M phosphate buffer solutions (PBS) with different pH values were used to study the pH effect. All the solutions were prepared with double distilled water.

2.2. Apparatus

The anodization of the stainless steel (SS) electrode was performed using a DC power supply (Esfahan Tak, Iran). Cu electrodeposition and all the electrochemical measurements were carried out using an Autolab potentiostat-galvanostat, Model PGSTAT302 (Echo Chemie, The Netherlands) in a conventional three-electrode cell at room temperature (25 ± 2 °C). The system was run on a PC using GPES and FRA 4.9 software. The counter and reference electrodes were a platinum rod electrode and a saturated Ag/AgCl reference electrode, respectively. A modified or unmodified SS rod electrode or a smooth poly-crystalline gold electrode (GE) was used as the working electrode. The SS electrode was a 304 type rod with a diameter of 0.30 cm which was embedded in Teflon to leave a cross-sectional available area of 0.07 cm^2. The electrochemical impedance spectroscopy (EIS) measurements were performed by applying an appropriate polarization potential with ac voltage amplitude of 5 mV in a frequency range from 100 kHz to 10 mHz. A pH-meter (Coring, Model 140) attached to a double junction glass electrode was used to control the pH values of the solutions.

A field emission scanning electron microscope (FESEM, Hitachi S4160) operated at an accelerating voltage of 20.0 kV and an energy dispersive X-ray spectrometer (EDX) attached to a Seron technology scanning electron microscope (SEM, model AIS2300C) were used to characterize the surface of the electrodes. Atomic force microscopy (AFM) images were used using an atomic force microscope (BRUKER, Germany).

2.3. Electrode preparation

Before anodization, SS was mechanically polished with 1000 grit water proof abrasive paper, and then sonicated in 2 M HNO_3 for 10 min. Afterwards it is polished with 0.05 μm alumina slurry on a polishing cloth, and then washed ultrasonically in ethanol and distilled water (1:1, v/v) mixture.

The SS electrode was anodized using the procedure described in the literature [11,29]. Accordingly, a constant voltage of 35.0 V was applied between the SS electrode (anode) and a flat copper plate (cathode) immersed in a vigorously stirred ethylene glycol electrolyte containing 5 vol.% $HClO_4$ for 15 min. During the anodization process, the electrolyte temperature was maintained in the range of 0–5 °C and the distance between the anode and cathode was 1.0 cm. The obtained nanoporous stainless steel electrode (NPSS) was washed ultrasonically in a mixture of ethanol and water (1:1, v/v) for 10 min and then dried at room temperature.

Afterwards, the pulsed electrodeposition technique was used to fill the nanopores of the NPSS with Cu as has been explained in our previous work [11]. Briefly, NPSS was immersed into a dearated 30 $g\,L^{-1}$ boric acid solution containing 10 $g\,L^{-1}$ $CuSO_4{\cdot}3H_2O$ and then a triple-potential pulse sequence consists of a cathodic pulse potential of −5.0 V, an anodic pulse potential of 0.1 V and a delay time was applied continually for 9 times. The pulse time for cathodic, anodic and delay time was 4, 26 and 900 ms, respectively.

After the Cu electrodeposition step, the substrate was immersed immediately into a 1.0 mM $HAuCl_4{\cdot}3H_2O$ solution at room temperature to perform the galvanic replacement reaction. The obtained electrode is named Au/NPSS electrode.

2.4. Preparation of DA injection solution and biological fluid samples

An injection solution of DA with the commercial name of Dopadic was purchased from Caspian Tamin Pharmaceutical Co. (Rasht, Iran). The solution, which contains 40 $mg\,mL^{-1}$ dopamine hydrochloride, was diluted with water to obtain a 10.0 mM