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Sonoelectrodeposition of gold nanorods at a gold surface – Application for electrocatalytic reduction and determination of nitrofurazone

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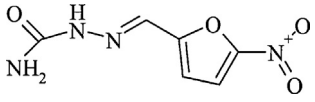
ABSTRACT

A sensitive electrochemical sensor was designed based on gold nanorods synthesized by a sonoelectrodeposition method. The morphology and structure of the nanorods were investigated, and voltammetric measurements were performed to study the kinetics of nitrofurazone electroreduction on the nanorod surface in a pH 7.40 phosphate buffer solution. Nitrofurazone was electroreduced on the nanorod surface at lower potentials with a higher rate, compared to a polycrystalline smooth gold surface, through an irreversible process. The results showed that the nanorods can be utilized to fabricate a nitrofurazone sensor. Amperometric and differential pulse voltammetric procedures were applied to the determination of nitrofurazone. Linear dynamic ranges of 50–610 and 3.0–500 μmol L^{-1} with calibration sensitivities of 2.02 and 0.5 A L mol^{-1} cm^{-2}, and detection limits of 6.51 and 0.18 μmol L^{-1} were obtained using amperometry and differential pulse voltammetry (DPV), respectively. DPV method was applied to the analysis of nitrofurazone ointments, and the applicability of the method to direct assays of spiked human serum and urine fluids was investigated.

1. Introduction

Drug analysis plays an important role during various phases of pharmaceutical developments, including formulation, monitoring and control, and stability, toxicology and pharmacological studies [1–3]. This involves analysis of patient samples for bioavailability and pharmacokinetic studies [4,5]. In order to achieve such purposes, reliable and validated analytical methods for measuring drugs in different media are desirable. Electroanalytical methods for drug analysis offer the advantages of permitting a direct, simple and rapid determination route requiring a minimum volume of sample. Electroanalytical techniques will also enable to study the drug reaction mechanisms at an electrode, which can provide insight into their metabolic fate, in vivo redox processes and pharmacological activities [6,7].

Nitrofurazone (5-nitro-2-furaldehyde semicarbazone, Scheme 1) is a synthetic nitrofuran derivative reported to possess good bacteriostatic and bactericidal properties, with an antibacterial action against a number of gram-negative and gram-positive microorganisms [8,9]. It is also used for treatment of burns [10] and trypanosomiasis [11]. In veterinary medicine, nitrofurazone is used for the treatment and prophylaxis of coccidiosis in poultry and farm animals, and necrotic enteritis in pigs [8].



Scheme 1. Chemical structure of nitrofurazone.

A variety of techniques has hitherto been proposed for assay determination of nitrofurazone. These include spectrophotometry [12,13], paper chromatography [14], liquid chromatography [15], liquid chromatography–mass spectrometry [16], liquid chromatography–tandem mass spectrometry [17], high performance liquid chromatography (HPLC) [13,16,18,19], and electroanalytical methods [20–23]. However, some of these methods suffer from several pitfalls, such as sensitivity, long run time, fouling electrode surface, high overpotential requirement, or a cumbersome extraction procedure before analysis, which prevent their use for routine sample analysis. For example, some detection methods in HPLC technique have exhibited low sensitivity [24,25] and require relatively large sample volume [26,27], complicated sample

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preparation procedures including evaporation steps [27,28], long chromatographic times [29], long analytical columns and conventional mobile phase flow rates [24–29].

Recent developments in nanotechnology research are accompanied by the synthesis of new nanostructured materials with novel properties [30]. These nanostructured materials offer excellent electronic, conductivity and catalytic properties, and electrocatalytic activity, which accelerate electron transfer between electrode surface and redox species. These nanostructured materials have been applied to electroanalysis of drugs in various preparations and in biological fluids [31–35]. The design and synthesis of nanostructures on electrode surfaces have been performed to improve sensitivity of electrochemical measurements by increasing the surface area or using the catalytic activity of nanosized materials [31–38].

The incorporation of nanostructures on an electrode surface has been largely considered for diverse analytical applications [31–40]. Among them, gold nanostructures exhibit unique physicochemical properties, making them increasingly applied to fabrication of chemical and biological sensors [41]. Although gold nanoparticles have been widely used for electrochemical sensing, gold nanorod-based platforms can provide more stable sensing systems, compared to the gold nanoparticles [42]. In addition, gold nanorods are a class of useful gold nanostructures because of the interesting properties derived from their strong-length dependent surface plasmon resonance absorption in the near-infrared region and one-dimensional morphology for nanoscale assembly applications [43–45].

In the present study, gold nanorods were sonoelectrodeposited on a gold surface for the first time, and then applied to the electrocatalytic reduction and determination of nitrofurazone. To the best of our knowledge, this approach has not been carried out successfully so far. Gold nanorods with a special structure can show high activity along the long axis. Therefore, it can be employed for electroreduction of different substances and development of various electrochemical sensors.

2. Experimental

2.1. Materials

All chemicals were of analytical grade form Merck (Germany) or Sigma (USA) and were used without further purification. Nitrofurazone was received from Behvazan, Iran. The nitrofurazone ointments were obtained from a local drugstore. All solutions were prepared using redistilled water.

2.2. Apparatus

Electrochemical measurements were carried out in a conventional three-electrode cell powered by an μ-Autolab potentiostat/galvanostat (Utrecht, the Netherlands). An Ag/AgCl, 3 mol L^{-1} KCl reference electrode, a glassy carbon wire counter electrode, and a bare gold (Au) or modified gold disk working electrode (all form Azar Electrode Co., Iran) were used. The system was run on a PC by GPES 4.9 software. In order to obtain information about the morphology and size of gold nanorods, field emission scanning electron microscopy (FE-SEM) was performed using a Zeiss, Sigma-IGMA/VP (Germany).

2.3. Procedures

Before electrodeposition of gold nanorods, the Au electrode was polished on a sand paper and then on a polishing pad with 50 nm-alumina powder lubricated by glycerin. Polishing was continued to attain a mirror-like Au electrode surface. The electrode was then cleaned by immersing it in a 1:3 water/ethanol mixture and ultrasonication for 5 min in an ultrasound bath. The electrode was further electropolished by conducting 25 consecutive cyclic voltammetric scans in a 500 mmol L^{-1} H_2SO_4 solution between the cahodic and anodic potential limits. Upon this treatment, a clean and stable Au electrode surface was attained. The Au electrode was then placed in the cell containing the synthesis solutions comprising 5 mmol L^{-1} $HAuCl_4$ + 0.5 mol L^{-1} KCl. Sonoelectrodeposition of the gold nanorods was performed at 300 mV for 500 s, while the synthesis solution and also the Au electrode surface were irradiated by ultrasound wave of 45 W power. The gold nanorods electrodeposited-Au (Au-AuNR) electrode was then rinsed thoroughly with distilled water.

The real surface areas of the Au and Au-AuNR electrodes were determined electrochemically using $K_4[Fe(CN)_6]$ (0.5 mmol L^{-1}) as a redox probe. For a reversible redox process, the peak current is [46]:

$$I_p = (2.69 \times 10^5) n^{3/2} A C^* D^{1/2} \nu^{1/2} \quad (1)$$

where I_p is the peak current, n is the number of exchanged electrons, A is the electrode surface area, C^* is the bulk concentration, D is the diffusion coefficient of the electroreactive species, and ν is the potential sweep rate. For the redox transition of $[Fe(CN)_6]^{4-}$, $n = 1$ and $D = 7.60 \times 10^{-6}$ cm s^{-1} [47]. Therefore, cyclic voltammograms using both Au and Au-AuNR electrodes were recorded and the real surface areas were obtained. The Au-AuNR electrode was estimated to be ~1.6 times larger in surface area than the Au electrode.

Standard solutions of nitrofurazone were prepared by dissolving the drug in a small volume of ethanol, and stored in the dark at 4 °C. Additional dilutions were performed daily just before use with 100 mmol L^{-1} Na-phosphate buffer solution, pH 7.40 (PBS). The drug solutions were stable and their concentrations did not change with time. For pH adjustment at different values, appropriate volumes of hydrochloric acid or sodium hydroxide solutions (100 mmol L^{-1}) were added to PBS. In all the studies, PBS was purged from oxygen by introducing a nitrogen (>99.99% purity) stream into the solution for 60 min. Degassed PBS was used as the supporting electrolyte throughout the studies.

The calibration curves for the drug in PBS were measured with amperometric and differential pulse voltammetric techniques. For amperometry, a working potential of −400 mV was applied, while, in it the transient currents were allowed to decay to steady-state values. For differential pulse voltammetry (DPV), a pulse width of 25 mV, a pulse time of 50 ms, and a scan rate of 10 mV s^{-1} were employed.

For analysis of the drug ointments, an exact weight of the ointment (0.5 g) was added to 5 mL ethanol (70% V/V) and mixed by a spatula. The mixture was then sonicated in an ultrasound bath for 10 min. After that, the mixture was centrifuged for 10 min at 3500 rpm. The supernatant was removed and the clear yellow solution was employed as a stock solution; appropriate volumes of this solution were diluted with PBS and directly analyzed.

The drug-free blood samples were obtained from healthy volunteers. The fresh samples were stored at 4 °C until formation of two phases. The supernatant phase was separated by centrifuge as the serum blood. The serum samples were stored frozen until being assayed. Various portions of stock nitrofurazone solutions were transferred into serum samples and then diluted to the desired volume with PBS for preparation of spiked samples (final dilution of 1:9). The spiked serum solutions were directly analyzed by DPV based on the calibration method.

Urine samples were taken from a healthy person and diluted with PBS (1:4), after adding appropriate amounts of nitrofurazone standard solution. The resulting solutions were then directly analyzed, according to the proposed procedure without any