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Electrooxidation and amperometric determination of vorinostat on hierarchical leaf-like gold nanolayers

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ABSTRACT

Hierarchical leaf-like gold nanolayers were electrodeposited using choline chloride as a shape directing agent and characterized using field emission scanning electron microscopy. The electrooxidation behavior of vorinostat was then studied on the nanolayers and the kinetic parameters of the electrodic process were obtained by voltammetric measurements in a phosphate buffer solution at pH 7.40. Vorinostat was electrooxidized on the nanolayers' surface at a lower potential and with a higher rate, compared to a polycrystalline smooth gold surface, through an irreversible process. Based on the results, an amperometric sensor was designed using the hierarchical leaf-like gold nanolayers for the determination of vorinostat. A linear dynamic range of 4.0–52 μmol L^{-1} with a calibration sensitivity of 7.7 mA mol^{-1} L, and a detection limit of 1.40 μmol L^{-1} were obtained. The amperometry method was also applied to the analysis of vorinostat capsules.

1. Introduction

Synthesis of new nanostructured materials with novel properties and diversities in shape and size is one of the most important recent developments in nanotechnology [1]. Nanomaterials have been extensively utilized in various field of nanomedicine including imaging [2], drug delivery [3], diagnosis [4], therapy [5], antibacterial materials [6] and biosensing [7,8]. These materials cause to enhancements in sensitivity and selectivity of the sensing and biosensing methods [9–13] arising from their unique physicochemical properties related to the size, shape, atomic arrangement and the electronic and local dielectric specifications [14–17]. Therefore, the exact controlling size and shape are key parameters to control the physicochemical properties of nanostructures [16,18].

Study of the redox properties of biologically active compounds can give insight into their pharmacological activities, metabolic fate, their mechanism of action in vivo, and quantitation in pharmaceutical dosage forms and biological fluids [19,20]. In this regard, nanomaterials have attracted considerable attentions [21–23]. These materials have been successfully applied to the electroanalysis of drugs, pharmaceuticals and biologically important compounds [9,10,19,24,25].

Vorinostat (N-Hydroxy-N′-phenyloctanediamide, VOR, Scheme 1) is a synthetic hydroxamic acid derivative with antineoplastic activity. It binds to the catalytic domain of the histone deacetylases (HDACs) resulting in the hydroxamic moiety to chelate zinc ion in the active site of HDAC. This causes to inhibition of enzyme activity and hyperacetylation of histones. Hyperacetylation of histone proteins results in the upregulation of the cyclin-dependant kinase p21, followed by G1 arrest. This drug also sensitizes tumor cells to apoptosis. Vorinostat is administrated for the treatment of cutaneous T cell lymphoma, a type of skin cancer, to be used when the disease persists, gets worse, or comes back during or after treatment with other medicines.

There are a few reports on the determination of VOR [26–30] based on liquid chromatography-mass spectrometry which is generally complicated, tedious, expensive and time-consuming. In addition, no electrochemical study has been performed on VOR. In the present study, hierarchical leaf-like gold nanolayers were electrodeposited using choline chloride as the shape directing agent, and then applied to the electrocatalytic oxidation and determination of VOR. The methodology provides accuracy, precision and excellent limits of detection and quantitation, which are critical parameters in the analysis of a drug.

2. Experimental section

2.1. Materials

All chemicals were of analytical grade purchased form Merck (Germany) or Sigma (USA) and were used without further purification. VOR was received from Arasto Pharmaceutical Chemicals Inc., Tehran, Iran.

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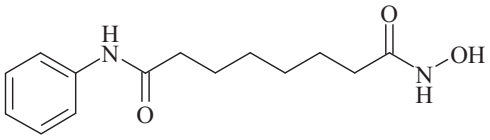

Scheme 1. Chemical structure of VOR.

2.2. Apparatus

Electrochemical experiments were performed in a conventional three-electrode cell powered by a μ-Autolab type III potentiostat/galvanostat (The Netherlands). An Ag/AgCl-saturated solution of KCl, a glassy carbon rod, and a bare (Au) or modified gold disk electrode with the hierarchical leaf-like gold nanolayers (Au/LN-Au) were used as the reference, counter and working electrodes, respectively. The system was run on a PC through the GPES 4.9 software.

In order to obtain information about the morphology and size of the synthesized gold nanostructure, field emission scanning electron microscopy (FESEM) was performed using a Zeiss, Sigma-IGMA/VP instrument (Germany) equipped with energy dispersive X-ray spectroscopy (EDS) capability.

2.3. Modification of the Au electrode with the leaf-like gold nanolayers

Au/LN-Au electrode was prepared by a potentiostatic electrodeposition method. Firstly, the Au electrode was polished by sand papers and then on a polishing microcloth with 0.05 μm-alumina powder lubricated with water to attain a mirror-like surface. The electrode was then cleaned by immersion in a 1:3 water/ethanol mixture and ultrasonication for 5 min in an ultrasonic bath. The electrode was then electropolished by immersion in a 500 mmol L^{-1} H_2SO_4 solution and applying potential in the range of cathodic to anodic edges of the

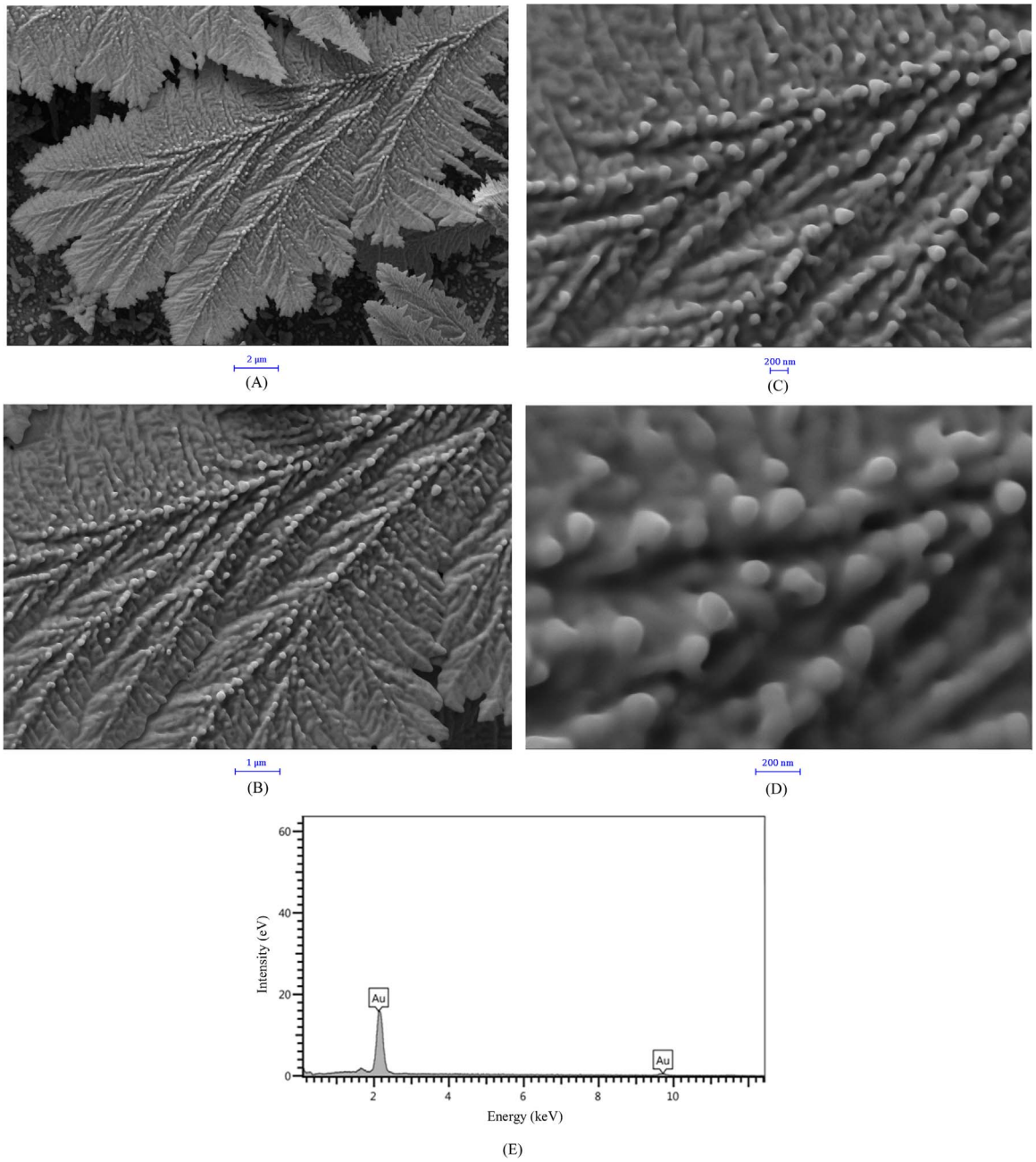

Fig. 1. FESEM images (A-D) with different magnifications and an EDS (E) of the Au/LN-Au electrode surface.