



Electrocatalytic quantification of antitubercular drug ethionamide in sodium lauryl sulfate



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ABSTRACT

A novel voltammetric sensor has been developed with zirconia nanoparticles by drop casting method. Sensor was characterized with scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. Electrochemical impedance spectroscopic (EIS) spectra exhibited decrease in charge transfer resistance, which indicates the good conductivity of the modified sensor as compared to bare glassy carbon electrode. Voltammetric behavior of ethionamide (ETA) on the developed sensor was investigated by cyclic voltammetry (CV) and square-wave voltammetric (SWV) methods and results indicated that the electrode process is diffusion controlled. Under optimized conditions, the peak current in SWV, increased linearly with the ethionamide (ETA) concentration in the range of 150–650 ng/mL and a limit of detection (LOD) was found to be 47.66 ng/mL.

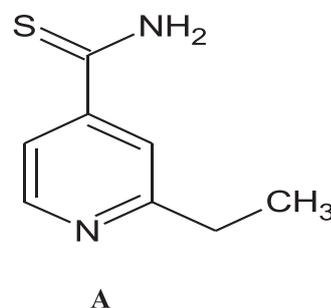
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1. Introduction

Electrochemical sensors have many potential applications in various fields including medical diagnosis, pharmaceuticals and environmental analysis [1–3]. Performance of a voltammetric sensor is dependent upon the electrode material. Zirconia nanoparticles (ZrO₂) have been used as electrodes for various electrochemical sensors due to their excellent chemical inertness, high electrical conductivity, lack of toxicity and low background current. These characteristics lead to high stability, low detection limit and a significantly improved signal to noise (S/N) ratio [4–6]. ZrO₂ is of great interest due to their improved optical and electronic properties with application as a piezoelectric, electro-optic and dielectric material [7]. Zirconium oxide modified glassy carbon electrode have been used for the detection of various bio molecules such as hemoglobin, cytochrome P450 2B6 and DNA etc. [8–10]. To the best of our knowledge, no systematic report is available on the zirconia based voltammetric sensor in solubilized system.

Ethionamide (2-ethyl thioisonicotinamide, ETA) is a nicotinamide derivative and structural analog of isoniazid (A). Few methods have been available for the quantification of ETA in serum/plasma using

HPLC with UV detection as well as LC/MS [11,12], RP-HPLC [13] and solid phase extraction (SPE) [14]. The above mention methods suffer from difficult extraction procedure, interferences, poor sensitivity and detection limit.



It has been seen that surfactants have great significance in electrode reactions, not only in solubilizing organic compounds but also in providing specific orientation of the molecules at the electrode surface and have been used in electrochemical investigations [15–17]. Chemically modified electrodes and surfactants have been widely used for electrochemical studies [18–32].

Present paper reports electrocatalytic quantification of ETA using cyclic voltammetry (CV) and square wave voltammetry (SWV) at fabricated ZrO₂/GCE based sensor in solubilized system.

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2. Materials and methods

2.1. Reagents and solution preparations

Zirconia (12 nm) was obtained from Sigma Aldrich. Ethionamide (ETA) standard (99.7% purity) was provided by Jubilant Clinsys (India). ETA Tablets containing ETA (Ethomid®) manufactured by Macleods Pharmaceuticals Ltd. (India), were purchased from commercial sources. Surfactants and all other chemicals were obtained from Sigma–Aldrich or Merck. Ultra-pure water, obtained from Milli-Q purification system (Millipore Corp., Milford, MA, USA), was used throughout the studies. All experiments were carried out at the room temperature of the laboratory.

2.2. Measurements and apparatus

Cyclic voltammetry (CV), square-wave voltammetry (SWV) and electrochemical impedance spectra were obtained with a μ Auto-lab Type III (Eco-Chemie B.V., Utrecht, The Netherlands) potentiostat–galvanostat and 302N Auto-lab potentiostat–galvanostat (Netherlands). A three-electrode cell was employed consisting of working electrode (bare GCE or zirconia modified GCE, 3 mm in diameter), an Ag/AgCl (saturated KCl) reference electrode and a platinum rod as a counter electrode. A systronics digital μ pH meter model-361 was used for pH meter measurements. All experiments were performed at room temperature and dissolved oxygen was removed by passing pure nitrogen through the solutions for 10 min. Scanning electron microscopy (SEM) image was obtained from Zeiss EVO 50 SEM. XRD analysis was done on a Seifert XRD 3003 PTS diffractometer with Cu K α radiation ($\lambda = 1.5418\text{Å}$).

2.3. Preparation of the zirconia modified GCE

The bare GCE was polished with 0.5 μm alumina powder, followed by ultrasonic rinsing with 1:1 HNO₃:water, ethanol and deionized water respectively and dried at room temperature. Zirconia was dispersed in DMSO (2 mg/mL) with ultra-sonication for 30 min. 4 μL of Zirconia suspension was deposited on the surface of GCE using micro syringe and dried at room temperature to obtain the ZrO₂/GCE sensor. Prior to use the modified electrode was carefully rinsed with water to remove the loosely attached zirconia at the electrode and dried in an air stream.

3. Results and discussion

3.1. Characterizations of fabricated sensor

3.1.1. Surface characterization of ZrO₂/GCE

Fig. 1A depicts the SEM image of the ZrO₂. The morphology of the zirconia consisted mostly of ovalar and irregular shape.

The XRD pattern of zirconia nanoparticles is shown in Fig. 1B, the diffraction peaks are absorbed at 2θ ranges between 10° and 70°. X-ray diffraction patterns of the pure ZrO₂ nanoparticles exhibit two sharp diffraction broad peaks at scattering angles at 28.29° and 31.57, corresponding to the inter-planar spacing of 3.1 Å and 2.8 Å, which indicates that zirconia is crystalline in nature.

3.1.2. Electrochemical impedance spectroscopy of zirconia nanoparticles

A Nyquist diagram of electrochemical impedance spectrum is an effective way to measure the electron-transfer resistance. Fig. 2 shows Nyquist plots of bare GCE and ZrO₂/GCE in the presence of 1 mM [Fe(CN)₆]^{3-/4-} probe at pH 7.4 phosphate buffer solution. EIS was recorded to understand the properties of the ZrO₂ film in the electrochemical process of ETA. The electrocatalytic behavior of zirconia was confirmed by the reduction of charge transfer resistance in electrochemical impedance spectra. Equivalent circuit values of charge transfer resistance were found to be 62.9 k Ω at GCE, 42 k Ω at ZrO₂/GCE. This

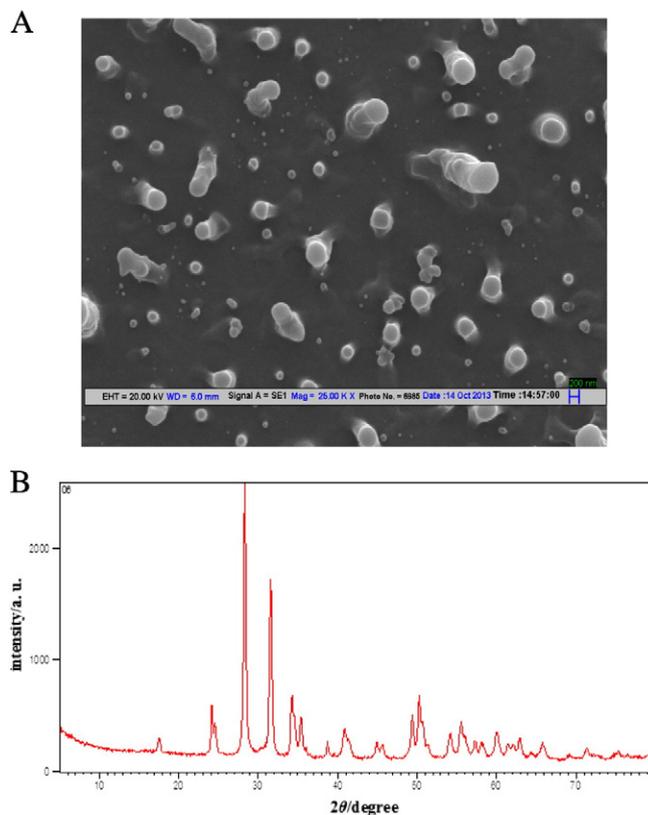


Fig. 1. SEM (A) image of ZrO₂/GCE and XRD (B) pattern of ZrO₂.

data confirm the enhancement of electron transfer rate of redox species Fe(CN)₆^{3-/4-} at ZrO₂/GCE, suggesting that the charge transfer through the surface of ZrO₂ modified electrode was facile in comparison to bare electrode.

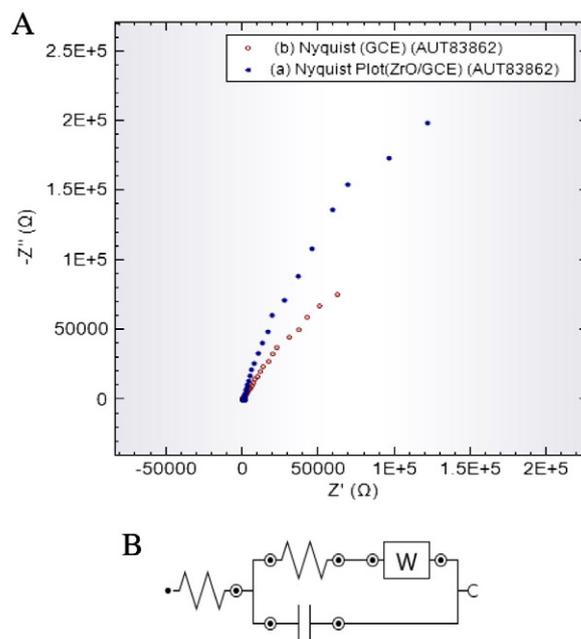


Fig. 2. Nyquist plots of 1 mM Fe(CN)₆^{3-/4-} in 0.01 M PBS at GCE (A, curve b), ZrO₂/GCE (A, curve a), frequency range is from 0.5 Hz to 100 kHz. The ac amplitude of 5 mV was applied and corresponding equivalent circuits were used for the determination of charge transfer resistance (B).

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