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## ORIGINAL ARTICLE

# Applied electrochemical biosensor based on covalently self assembled monolayer at gold surface for determination of epinephrine in the presence of Ascorbic acid

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**Abstract** In this paper, a new electrochemical sensor for the determination of epinephrine (Epi) in the presence of ascorbic acid (AA) is described. The characterization of Au TMBH self-assembled monolayer modified electrode (TMBH SAM-ME) was investigated by cyclic voltammetry (CV) using the  $[\text{Fe}(\text{CN})_6]^{-3/-4}$  redox couple. The mediated oxidation of Epi at the modified electrode was investigated by voltammetric methods and the values of transfer coefficient ( $\alpha$ ), the ionic exchanging current density ( $i_0$ ), catalytic rate constant ( $k_h$ ) and diffusion coefficient ( $D$ ) were calculated. By double potential step chronoamperometric experiments (DPCHA) at the modified electrode was obtained two linear segments of 1.7–24.9  $\mu\text{M}$  and 24.9–91.7  $\mu\text{M}$  by a detection limit ( $3\sigma$ ) of  $0.19 \pm 0.01 \mu\text{M}$  for Epi. The advantages of this modified electrode were reproducibility and repeatability, stability and anti fouling effect against oxidation products of Epi at the surface of TMBH SAM-ME. Finally, the modified electrode was shown agreeable responses to recovery of Epi from real sample solutions by standard addition method.

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## 1. Introduction

Chemical modification of the electrode surface is of great importance in electrochemistry including a wide spectrum of promising applications. In particular, thin films and self-assembled mono layers (SAMs) have been used in electro analytical chemistry for the modification of the electrodes to develop sensors (Shervedani et al., 2008; Shervedani and Mozaffari, 2006) and biosensors (Shervedani et al., 2006; Shervedani and Mehrjardi, 2009). Further modification of the SAMs may allow fabrication of highly sensitive and more sophisticated sensors and biosensors for trace analysis.

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Schiff bases, named after Hugo Schiff, are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions. Structurally, a Schiff base (also known as imine or azomethine) is a nitrogen analog of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine group (Raman et al., 2009). Schiff bases are some of the most widely used organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis, and as polymer stabilizers. Schiff bases have also been shown to exhibit a broad range of biologic activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties (De Souza et al., 2007; Guo et al., 2007). The imine group present in such compounds has been shown to be critical to their biologic activities. The applications in electrochemistry, bioinorganic, biosensors, antimicrobial activity, fluorescence properties, catalysis, metallic deactivators and separation processes are reported for these components (Joseyphus and Nair, 2009).

The electrochemical impedance spectroscopy (EIS) is a powerful, nondestructive and informative technique, which is usually used for characterization and study of corrosion phenomena (Mansfeld and Lorenz, 1991), fuel cells and batteries (Lasia, 1999), coatings and conductive polymers (Inzelt and Lang, 1994), adsorption behavior of thin films (Benavente et al., 1996), the SAMs (Janek et al., 1997) and electron transfer kinetics (Protsailo and Fawcett, 2000). Recently, the EIS has been used in analytical chemistry to trace modification steps of chemically modified electrodes based on SAMs and to quantify the inorganic (Shervedani and Mozaffari, 2005) or biologic (Janata, 2002) species in solution.

To our knowledge, there is no report on the electrocatalytic determination of Epi in the presence of AA using SAM modified gold electrodes (SAM-Au). Thus, in the present work, 2-hydroxy-N'1-(E)-1-(3-methyl-2-thienyl) methylidene] benzohydrazide (TMBH) as a Schiff base, which is a bio mimetic analog, was chosen to form Au-TMBH SAM modified electrode. The structural integrity and compactness of the modified surface were then investigated by characterization of the electrode in the presence of a reversible redox reaction probe. The investigations were aimed at evaluating the anti-fouling performance of this monolayer as a suitable sensor material for the analysis of neurotransmitters like Epinephrine (Epi). Finally, the proposed Au-TMBH SAM electrode was successfully examined for determination of Epi in a real sample.

## 2. Experimental

### 2.1. Chemicals and apparatus

2-hydroxy-N'1-(E)-1-(3-methyl-2-thienyl) methylidene] benzohydrazide (TMBH), has been synthesized in inorganic laboratory of the University of Kashan and characterized by physical and spectroscopic data. Epinephrine and other materials used in this work were of analytical grade (Merck®) and used without further purification.

The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on Auto lab Potentiostat/Galvanostat, PGSTAT 35 (Eco chemie Utrecht, Netherlands), equipped with the General Purpose Electrochemical System (GPES 4.9,006 software) and NOVA,

in a conventional three electrode glass cell containing polycrystalline gold disk (Metrohm, 2 mm diameter) as a working electrode, a Pt plate (99.99%, 5 cm<sup>2</sup>) as an auxiliary electrode, and a Ag/AgCl (3 M KCl) as the reference electrode.

### 2.2. Synthesis of TMBH

The thiol Schiff-base; TMBH, was synthesized in the usual manner by reaction of 3-methyl-thiophene-2-carbaldehyde with salicylhydrazone in a 1:1 M ratio in methanol as follows. 3-methyl-thiophene-2-carbaldehyde (0.01 mol, 1.26 g) and salicylhydrazone (0.01 mol, 1.52 g); were placed in 100 mL round-bottomed flask equipped with a condenser and a magnetic bar. Methanol (50 ml) was then added to the mixture and the mixture was refluxed for 3 h while stirring, and then cooled to room temperature. The solid product was filtered, and the product was recrystallized from ethanol. Analytical calculated for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S: C, 59.98; H, 4.65; N, 10.76%. Found: C, 58.17; H, 4.59; N, 10.88%; IR bands (KBr, cm<sup>-1</sup>),  $\nu_{C=N}$ , 1594 cm<sup>-1</sup>; Yield = 80%.

### 2.3. Electrode preparation

The polycrystalline gold disk electrodes were polished using aqueous slurries of alumina (0.3 down to 0.05  $\mu$ m, Buehler®), sonicated in water/chloroform/water for 5 min. Then, the gold working electrode was kept in Piranha solution (1:3, v/v; 30% H<sub>2</sub>O<sub>2</sub> and concentrated H<sub>2</sub>SO<sub>4</sub> [caution: Piranha solution is extremely corrosive and must be handled carefully]) for 3.0 min and rinsed thoroughly with double-distilled water and then cleaned electrochemically by cycling the electrode potential between 0.000 and +1.500 V vs. a reference electrode, with a 100 mV s<sup>-1</sup> scan rate in 0.5 M sulfuric acid and 0.000 until -1.400 V with a 100 mV s<sup>-1</sup> scan rate in 0.5 M NaOH until reproducible voltammograms were observed. A roughness factor of 3.25 was obtained for bare Au electrodes from the ratio of the real to geometric surface area (Oesch and Janata, 1983; Carvalho et al., 2005). Immediately prior to modification, the cleaned Au electrode was thoroughly rinsed with de ionized water, and placed into a 1.0 mM TMBH ethanol solution for 8 h to form Au-TMBH SAM electrode. Finally, after modification of gold electrode, the oxidation of Epi was investigated by electrochemical impedance spectroscopy and voltammetric methods such as cyclic voltammetry, linear sweep voltammetry, chronocoulometry and double potential step chronoamperometry at the surface of modified electrode. Finally, this electrode was tested for detection of Epi in human blood serum.

## 3. Results & discussion

### 3.1. Electrochemical characterization of the self assembled monolayer of TMBH

#### 3.1.1. Characterization of TMBH in H<sub>2</sub>SO<sub>4</sub> media

The CV of the bare-Au electrode and TMBH SAM-ME in 0.5 M H<sub>2</sub>SO<sub>4</sub> shows that the gold oxidation/reduction currents are suppressed at the TMBH SAM-ME in comparison with the bare-Au electrode. The electrode surface coverage ( $\theta$ ) is a key factor, which can be used to estimate the surface state of electrode. The surface coverage can be determined through a

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