



Electrocatalytic oxidation of NADH at low overpotential using nanoporous poly(3,4)-ethylenedioxythiophene modified glassy carbon electrode



Rajendran Rajaram, Sukeri Anandhakumar, Jayaraman Mathiyarasu *

Electrode and Electrocatalysis Division, CSIR-Central Electrochemical Research Institute, Karaikudi 630 006, Tamil Nadu, India

ARTICLE INFO

Article history:

Received 18 November 2014
Received in revised form 2 March 2015
Accepted 24 March 2015
Available online 24 March 2015

Keywords:

Nanoporous-PEDOT
NADH oxidation
Lower overpotential
Resistance to fouling
Without interference

ABSTRACT

Nanoporous-poly(3,4)ethylenedioxythiophene (PEDOT) modified glassy carbon electrode (GCE) significantly lowers the overpotential and shows high resistance against fouling while oxidizing β -nicotinamide adenine dinucleotide (NADH). The electrocatalytic behaviour of nanoporous-PEDOT modified GCE was studied using cyclic voltammetry in 0.1 M phosphate buffer solution (pH 7.0) containing 5 mM NADH. Studies revealed that nanoporous-PEDOT/GCE exhibited strong electrocatalytic activity on the oxidation of NADH with a decreased overpotential of about 0.318 V as compared to a bare GCE. In addition, chronoamperometric measurements were studied to understand the electron transfer kinetics of nanoporous-PEDOT/GCE which revealed an average diffusion coefficient (D) and apparent rate constant (k) of $1.56 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $1.09 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Sensitivity of nanoporous-PEDOT/GCE is measured by amperometric method which showed linear variation in the concentration range between 5 and 45 μM at an applied overpotential of 0.5 V. Limit of detection (LOD) and sensitivity are found to be 3.8 μM and 0.026 $\mu\text{A}/\mu\text{M}$, respectively. While quantifying the sensitivity of the electrode, it is found that the electrode surface fouling towards NADH oxidation decreased to an extent of 85%. Interference study is examined in the presence of ascorbic acid (AA) where a peak separation of more than 0.370 V is observed between AA and NADH. Thus, nanoporous-PEDOT/GCE provides a simple platform for the oxidation of NADH at low overpotential with high resistance against fouling and without AA interference.

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1. Introduction

β -Nicotinamide adenine dinucleotide (NADH) is involved in many dehydrogenase based enzymatic reactions as a cofactor to design electrochemical biosensors [1,2]. In order to use these applications, it is essential to develop electrodes which can effectively oxidize NADH and it has attracted enormous interest. However, the problem associated with NADH oxidation at conventional electrodes require large overpotential at which other electro active species are also present in the solution, compete in the oxidation process and they interfere NADH oxidation [3]. In addition, electrode fouling is also a concern, which is due to the adsorption of reaction products on the surface of the electrode. During the NADH oxidation, it produces NAD^+ which forms dimers and other oxidized products [4–6]. In order to diminish these deleterious effects, redox active mediators are often introduced to reduce the

overpotential [7,8]. Though mediators are effective for electron transfer in the immobilized or confined electrode surface, their toxicity, lack of stability and leakage from the electrode surface limits their analytical applications. Fujishima and co-workers reported that electrochemical oxidation of NADH at a boron-doped diamond electrode (BDD) which is known for its low background current and wide potential window [9]. Wang and co-workers reported that carbon nanotubes (CNTs) modified electrode exhibits very good electrocatalytic behaviour by lowering NADH oxidation overpotential and displayed high resistance against fouling [10]. Recently, nitrogen and boron doped carbon nanotubes [11,12] are reported for the oxidation of NADH. Other modified electrodes were also reported that includes edge-plane pyrolytic graphite [13], nitrogen doped diamond nanowire [14] electro-grafted o-aminophenol film [15], functionalized graphene [16] and gold nanoparticles [17]. Though different types of modified electrodes are reported for the oxidation of NADH, still there is a demand for novel electrode materials which can minimise overpotential, electrode fouling and avoiding interference from ascorbic acid (AA).

* Corresponding author.

E-mail address: al_mathi@yahoo.com (J. Mathiyarasu).

In recent years, poly(3,4)ethylenedioxythiophene [PEDOT] modified glassy carbon electrodes are used for the determination of biomolecules such as ascorbic acid, dopamine, and uric acid [18–20]. Vasantha et al. and Mahesh et al. reported the synergistic effect of catechin-immobilized poly(3,4)ethylenedioxythiophene modified electrode and gold nanoparticles loaded poly(3,4)ethylenedioxythiophene-poly(styrene sulfonic acid) film modified electrode respectively for NADH oxidation [21,22]. However, the main focuses in those works involve the immobilization of catechin mediator and gold nanoparticles on PEDOT matrix. Further, the electrode modification is attained by depositing PEDOT film from an aqueous solution or drop casting the PEDOT-PSS ink, which leads to increase in the film resistance and uniformity. Further, the characteristics of PEDOT matrix for NADH oxidation are not investigated in detail. In this work, the oxidation of NADH using nanoporous-poly(3,4)ethylenedioxythiophene modified GCE is reported, in order to achieve a low overpotential and high fouling resistance. Further, the electron transfer kinetics and effect of interference from other biomolecules such as ascorbic acid while oxidizing NADH is also investigated.

2. Experimental methods

2.1. Reagents

All the chemicals used in this work were of analytical purity. (3,4)ethylenedioxythiophene (EDOT), β -nicotinamide adenine dinucleotide reduced disodium salt hydrate (NADH), ascorbic acid (AA), tetrabutylammonium perchlorate (TBAPC) and acetonitrile were procured from Sigma Aldrich and used as received. Phosphate buffer solution (PBS) of pH 7.0 was prepared using 0.1 M sodium dihydrogen phosphate and 0.1 M disodium hydrogen phosphate. All aqueous solutions were prepared using Milli-Q water of 18.2 M Ω (Millipore), resistivity.

2.2. Apparatus

Cyclic voltammetry and amperometry measurements were carried out using CH instrument (1000A, USA) electrochemical analyser. A three-electrode system consisting of modified nanoporous-PEDOT/GCE, Ag/AgCl (3 M NaCl), and platinum foil are used as working, reference, and counter electrodes respectively. All measurements were performed at ambient temperature (25 \pm 1 $^{\circ}$ C). Field emission scanning electron microscopy (FE-SEM, TESCON model) was used to characterize the surface of nanoporous-PEDOT/GCE.

2.3. Preparation of nanoporous-PEDOT/GCE

GCE surface was polished on a fine polishing cloth using 1.0 and 0.05 μ m alumina powder and sonicated in Milli-Q water for 5 min. Before electro-polymerization, the polished electrode was pretreated by cycling it between -0.9 and 1.5 V vs Ag wire at 0.05 V s $^{-1}$ in acetonitrile solution containing 0.1 M TBAPC for 10 min. Afterwards, nanoporous-PEDOT was electrodeposited on the GCE surface using 0.01 M EDOT and 0.1 M TBAPC in acetonitrile solution by applying a constant potential of 1.5 V vs Ag wire as a pseudo reference electrode for 10 s.

3. Results and discussion

3.1. Mechanism and electrocatalytic activity of nanoporous PEDOT/GCE

The mechanism of EDOT polymerization is still under investigation; however the overall mechanism of electropolymerization is

depicted in Scheme 1A. During electrooxidation of EDOT monomer, a radical cation was produced then couples with a second radical cation to form a dication dimer or with another monomer to produce a radical cation dimer. Randriamahazaka et al. reported that the initial stage of electrodeposition was a combination of instantaneous 2D and 3D mechanisms since the electrodeposition was carried out under charge transfer control rather than diffusion [23]. Therefore, the attention is restricted to polymerize at the potential 1.5 V so that diffusion control will not be apparent and there by polymer growth was controlled resulting nanoporous PEDOT structure. Nevertheless, initially EDOT monomer gets oxidized in the solution and diffuses towards the electrode-solution interface, and beginning the oligomerization process. Once interface region is saturated with oligomers, deposition takes place onto the electrode surface forming “growing nuclei” that expands eventually to produce the desired film. Here, the PEDOT film has been found to follow 2D and 3D instantaneous growth of mechanism under potentiostatic conditions. Further, preparation of nanoporous PEDOT/GCE and its electrocatalytic activity are shown Scheme 1B. From the voltammetric experiments, a decrease in the anodic and cathodic peak separation (ΔE_p) was observed with appreciable increment in the oxidation/reduction current compared to bare GCE using $K_4[Fe(CN)_6]^{4-/-3-}$, a standard redox probe (Scheme 1B). This result clearly indicates the electrocatalytic nature of nanoporous PEDOT and it is further utilized for electrocatalytic oxidation of NADH at low overpotential.

3.2. Microscopic characterization of nanoporous-PEDOT/GCE

The FE-SEM images of electrodeposited nanoporous-PEDOT film on a GCE at different magnification is shown in Fig. 1. The images clearly signify a continuous PEDOT fibrillar network structure with a fibre dimension of ~ 20 nm. The polymer network exhibited highly porous structure with a pore size of ~ 25 – 100 nm, which is comparable with the observation of Jones et al. [24].

3.3. Electrochemical behaviour of nanoporous-PEDOT/GCE towards the oxidation of NADH

Fig. 2 shows the cyclic voltammetric response of bare GCE and nanoporous-PEDOT/GCE in 0.1 M PBS in the absence and the presence of 5 mM NADH at a scan rate of 0.05 V s $^{-1}$. Bare GCE exhibited a broad NADH oxidation wave, with a peak potential of 0.750 V. However, at a nanoporous-PEDOT modified GCE, the oxidation process starts at ~ 0.2 V and exhibit a sharp oxidation peak at 0.432 V revealed a substantial shift in the peak potential (0.318 V) towards less anodic direction with a two fold increment in the current signal. The shift in peak potential along with enhanced current signal can be reasoned as catalytic effect through electron transfer mediation. Conducting polymers are known to behave as electron mediators (PEDOT film has a rich electron cloud) that promote electron shuttling between the electrode surface and the electrolyte through their redox mediation. PEDOT polymer is electronically conducting in nature when it is in oxidized state and is selective to cations in the neutral form as reported by Higgins et al. [25]. Also the electrocatalytic activity of the polymer film arises from the formation of polarons, which is of positive charges on the polymer backbone. Therefore, a catalytic activity is revealed from the defined NADH oxidation peak at the nanoporous-PEDOT/GCE. The catalytic behaviour can also be revealed by the porous networked structure of PEDOT that may facilitate improved electron transfer process causes an enhanced current signal and hence the reaction occurs at lower overpotential [13].

The observed voltammetric response of electrochemical oxidation of NADH can be depicted as shown in Eq. (1).

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