



Study of electropolymerized PEDOT:PSS transducers for application as electrochemical sensors in aqueous media

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ARTICLE INFO

Keywords:

Robust PEDOT:PSS transducer
Electropolymerization deposition
Liquid media
Sensors

ABSTRACT

Electropolymerized poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) onto screen-printed platinum electrodes was tested for stable charge/discharge cycle using cyclic voltammetry (CV) in aqueous media and its adhesion to the electrode surface was also examined. Electropolymerized PEDOT:PSS maintained most of its initial CV behavior after water-flow test (flow rate = 1 ml/s), whereas drop-cast PEDOT:PSS did not, indicating better adhesion and retention of the polymer's mechanical and electrical properties. Field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDS) suggest that film structure influence the stability of the redox current measurements. These results prove that careful electropolymerization techniques for synthesizing the PEDOT:PSS transducer are worth pursuing in developing robust electrochemical sensors suitable for continuous use in aqueous media. Developing such transducers is important for developing electrochemical sensors for biomedical and/or environmental monitoring where aqueous flow usually occurs on electrode surfaces.

1. Introduction

Electrochemical sensors [1,2] are the most common type of sensing technology commercially available, owing to fast, simple, low-cost, real-time reading and applicability to a wide range of sample types [3–5]. Electrochemical biosensor performance relies on the ability of the receptor-transducer layer to transduce signal from a biochemical/chemical reaction or interaction to a measurable electrical signal [1,2]. The most common and commercially available electrochemical sensors are glucose sensors, representing 85% of the biosensor market as of 2004 [6–8]. These glucose sensors are sold as disposable strips as they are not suitable for continuous monitoring in aqueous media because the silver-silver chloride (Ag/AgCl) layer (active electrodes) requires constant replenishing of chloride ions to the material [9]. Hence, transducer layers with the following favorable characteristics are needed for the prolonged use of electrochemical sensors in aqueous media: (i) function in aqueous media without the need for frequent maintenance of electrodes; (ii) operate with stable charge-discharge profile; (iii) and display stronger adhesion to electrode surface.

To highlight these important properties, one can argue that if electrodes are made effective for prolonged use in liquid media, the glucose biosensor consumer model can shift from a one time-use disposable strip sensor, to that of multiple uses, or electrodes can be

developed into patches or semi-implantable devices that can provide continuous glucose monitoring. In addition, robust electrochemical electrodes are also suitable for environmental monitoring with the development of mobile sensors that can continuously monitor the environment (such as water and air quality) with minimal maintenance [10,11].

Poly(3,4-ethylenedioxythiophene): poly(styrene -sulfonate) (PEDOT:PSS), a conductive polymer (CP), is one of the better CPs commonly used in sensor development [12,13]. Thiophene-based materials such as polythiophenes (Tn) and poly ethylenedioxythiophene (EDOT)n and their derivatives have been widely investigated as they possess a wide range of interesting electrical and optical properties. In addition, the synthetic chemistry of thiophenes is well-developed, a feature that has allowed for facile preparation and subsequent investigation of numerous structures and studies of their properties. Suzuki and Stille coupling reactions have been widely utilized in these investigations. Synthetic flexibility has made systematic studies on series of structurally related thiophene-based polymers possible and has given them an advantage over other organic conducting polymers [14–17].

In particular for sensor applications, these materials are attractive as electrochemical sensor transducers owing to their easily-modified physicochemical properties, biocompatibility, and easy surface

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modification and functionalization, while retaining electrical conductivity; thus, they are excellent for applications in electronic and optoelectronic sensing systems [18,19]. Furthermore, PEDOT:PSS is attractive for electrochemical sensors owing to the reversible charge/discharge ability from the doping/de-doping of the polymer chain [20–22].

The high sensitivity of PEDOT:PSS to ionized species in aqueous media makes it one of the most used polymers in organic electronics [12,23]. However, these advantages of PEDOT:PSS are not without any limitations; the presence of PSS acting as a dopant to stabilize PEDOT:PSS results in PEDOT:PSS being highly hydrophilic and having an appreciable degree of water solubility which in turn leads to PEDOT:PSS film degeneration and peeling off easily from the surface of electrodes, while at the same time affecting the electrical conductivity, limiting its use in aqueous media [24,25].

Cyclic voltammetry is a common technique to measure the charge/discharge process of PEDOT:PSS, where current is measured with applied potential at a set scan rate (mV s^{-1}). During oxidation or reduction, ions move in and out of the PEDOT:PSS layers, and current is being measured at the electrode through transduction [26]. During the repeated charge/discharge process, the film undergoes volume change (swelling, shrinkage, cracking) as a result of dopant entering and leaving of the film. Thus, the ability of the film to withstand repeated charge-discharge cycle without degeneration in the CV profile and the mechanical integrity of the film are indicators of the film's ability to withstand prolonged measurements in aqueous media [25,27]. As such, CV can be a powerful technique to shed light on the mechanical and electrical stability and durability of sensors.

Besides adhesion of the PEDOT:PSS film to the electrode surface and the charge/discharge cycles, it is important to note that the morphology of PEDOT:PSS at the nanometer scale has a significant effect electrochemically. Studies show that although the shape of CV curves are almost the same for the same material at the same scan rate, the morphology affects the integrated area of the CV, suggesting that electron-transfer capability is highly dependent on the morphology of the film [28].

Numerous efforts have been made to improve the conductivity, structural integrity, and electro-chemical performance of conductive polymers like PEDOT:PSS for sensing purposes; one is to make the PEDOT:PSS less hydrophilic [29] by forming PEDOT:PSS composites with carbon-based materials such as carbon nanotubes (CNTs) and graphene to increase conductivity [30], and adding a binder like Nafion, polyvinyl alcohol (PVA), and/or sodium carboxymethyl cellulose (Na-CMC) to improve adhesion to electrode surfaces [25,27,31]. The method of film deposition is an important factor as well and can influence the conductivity, structural integrity, and electrochemical performance of PEDOT:PSS.

A PEDOT:PSS dispersion can be deposited on solid substrates through ink-jet printing [12,13] or drop-cast on commercialized glassy carbon electrodes (GCEs) or screen-printed electrodes (SPEs) [32,33]. Drop-casting remains a popular technique because of the simple fabrication process, but we think that it is suitable only for a disposable, one time-use biosensor, like the common commercial glucose sensor strips, and not suitable for monitoring purposes, especially when measurements are made in aqueous media. Furthermore, especially for environmental applications, water flow on the electrode surface can cause continuous stress on the film, and can result in deterioration of sensor performance.

Electropolymerization of 3,4-ethylenedioxy-thiophene (EDOT monomer) in poly(styrene sulfonate) solution is a common deposition technique whereby conductive electrodes oxidize the EDOT monomer in a complex electrolyte solution to produce radical cations that combine with themselves to yield higher oligomers with increasing molecular weight [19,34]. The resulting PEDOT:PSS composite obtained from the electropolymerization process is insoluble in water and has high electrical and ionic conductivity [23].

In this study we set to study of electro-polymerized PEDOT:PSS transducers for application as electrochemical sensors in aqueous media by investigating the study the film morphology as well as its CV behavior to establish a better understanding or provide insights into how morphology affects the CV characteristics. Our work focuses on characterization of CV charge-discharge cycles for PEDOT:PSS electro-polymerized on platinum electrodes as an indication of the stability of PEDOT:PSS in aqueous solution and also as an indicator for film adhesion in water. In view of the need for continuous monitoring in biomedicine and the environment [35–38], considerable research focuses on improving PEDOT:PSS adhesion to electrodes [25,27]; however, our research aims further to understand the stability and adhesion of PEDOT:PSS on electrodes under static and water-flow conditions as well as after prolonged storage in aqueous media, by comparing CV and surface characterization results for electrodes prepared via drop-casting (DC) to results for those prepared via electropolymerized deposition (EPD). Our results could provide insights regarding the applicability of PEDOT:PSS for developing electrochemical sensors for continuous use in aqueous media; this is particularly important for applications in glucose or environmental monitoring.

2. Materials and methods

2.1. Apparatus and reagents

A three-electrode cell system and platinum (Pt) three-electrode strips ($r = 1 \text{ mm}$) were purchased from Pine Instrument, Grove City, PA, USA. Electrochemical characterization of electrodes coated with PEDOT:PSS as the transducer material were performed using a pocketSTAT (IVIUM Technologies, Eindhoven, the Netherlands). PEDOT:PSS solution (1.3% w/w), 3,4-ethylenedioxythiophene (EDOT) monomer and poly(sodium 4-styrenesulfonate) (NaPSS) dopant, lithium perchlorate powder (LiClO_4 as supporting electrolyte), and potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$) were purchased from Sigma-Aldrich, St. Louis, MO, USA. To mimic measurements in biological buffer conditions, phosphate-buffered saline solution (PBS, pH 7.1) was prepared using sodium chloride (NaCl) and potassium chloride (KCl), purchased from Sigma-Aldrich; disodium phosphate (Na_2HPO_4), monopotassium phosphate (KH_2PO_4), and 37% hydrochloric acid (HCl) were purchased from R&M Chemicals, Selangor, Malaysia. Deionized (DI) water was used throughout the experiments.

2.2. Fabrication of drop-cast and electropolymerized PEDOT:PSS on a platinum working electrode

To prepare PEDOT:PSS electrodes, two techniques were used in modifying the working electrode: drop-casting (DC) and electropolymerization deposition (EPD), (as shown in Fig. 1a and b). For DC, 1 μl PEDOT:PSS solution (1.3% w/w) was drop-cast onto the surface of a Pt working electrode (WE). For EPD the solution consisted of 1 ml NaPSS, 1 ml of 0.1 M LiClO_4 , and 0.5 ml of 97% EDOT, all in 17.5 ml of deionized water. Galvanostatic mode was used to electropolymerize EDOT and NaPSS to PEDOT:PSS. The current and potential settings for galvanostatic mode were 100 μA and 400 mV, respectively. PEDOT:PSS on Pt electrodes (PEDOT:PSS/Pt) was left to dry for 24 h at room temperature to remove solvents before measurements.

2.3. Characterization

2.3.1. Effective surface area calculation

CV was performed to evaluate the electron-transfer capabilities of the PEDOT:PSS-based electrodes by measuring the magnitude of the anodic peak current and to calculate the effective surface area (A) [39]. CV was conducted in 50 mM $\text{K}_3\text{Fe}(\text{CN})_6$ solution at the potential range of -300 mV to $+400 \text{ mV}$ and with varying scan rates of 20, 50, 100, and 150 mV/s. The reduction peak current (I_p) was determined by

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