Sensors and Actuators B 161 (2012) 549–555

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Inkjet-printed graphene-poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) modified on screen printed carbon electrode for electrochemical sensing of salbutamol

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ARTICLE INFO

Article history:
Received 4 August 2011
Received in revised form 13 October 2011
Accepted 31 October 2011
Available online 6 November 2011

Keywords:
Inkjet printing
Graphene-poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate)
Screen printed carbon electrode
Salbutamol
Electrochemical sensing

ABSTRACT

In this work, a simple and sensitive inkjet-printed graphene-poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (GP-PEDOT:PSS) on screen printed carbon electrode (SPCE) is developed for detection of salbutamol (SAL), a prohibited drug in sport. GP-PEDOT:PSS dispersed solution is prepared for use as an ink by one-step electrolytic exfoliation from a graphite electrode. GP-PEDOT:PSS layers are then printed on SPCEs by dimatrix inkjet material printer and their electrochemical behaviors are characterized. It is found that SAL oxidation peak responses of PEDOT:PSS modified and GP-PEDOT:PSS modified SPCE electrodes are approximately 30 and 150 times higher than that of unmodified SPCE, respectively. In addition, excellent analytical features with a wide dynamic range of 500 μM, a low detection limit (3S/N) of 1.25 μM and low matrices' interference in pharmaceutical samples have been achieved. Therefore, inkjet-printed GP-PEDOT:PSS SPCE is a promising candidate for advanced electrochemical sensing applications.

1. Introduction

Graphene is a two-dimensional nano-carbon material with a honeycomb lattice structure that exhibits exceptional physical, chemical and electronic properties. It is thus a potential candidate for a number of electronic applications including field-effect and single-electron transistors [1,2], memory devices [3], solar cells [4] and electrochemical sensors [4–10]. In particular, it is highly advantageous for electrochemistry due to its very large two-dimensional electrical conductivity, excellent electron transfer rate and huge specific surface area. Some recent studies have demonstrated that the electrochemical sensitivity of graphene based electrodes is superior to those of single-walled carbon nanotubes (SWCNTs) [9] and glassy carbon electrode (GCE) [10] because of its larger number of edge plane per unit mass. In addition, it is considered more practical than SWCNTs counterpart because it can be inexpensively produced from low-cost graphite with no metallic impurity [10]. Metallic impurities commonly found in CNTs can induce anomalous electrochemical reactions, causing serious interference problems.

Graphene may be synthesized by several methods including micromechanical cleavage, epitaxial growth via ultra-high vacuum graphitation, chemical synthesis through oxidation of graphite, chemical vapor deposition (CVD), solvothermal synthesis and electrolytic exfoliation [11]. Among these, electrolytic exfoliation is particularly promising because it can produce stable graphene nanosheets in aqueous solution at low cost and may easily be scaled up for large-scale production. Moreover, it is the most suitable route for the formation of graphene in conducting polymer matrix, which can be highly useful for electrochemical transduction and bio-receptor immobilization. Conducting polymers including polythiophene [12], polyaniline [13] and polypyrrole [14] have also attracted much interest in electroanalysis due to their good electrical conductivity and electrochemical stability.

Poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) acid (PEDOT:PSS), an important derivative of polythiophene, is an attractive working electrode material for electroanalysis because of its high conductivity, low redox potential, high electrochemical, ambient and thermal stability [15]. PEDOT:PSS may be deposited on a transducer surface by solvent casting, dip coating, spin coating or inkjet printing [15–17]. Inkjet-printing technology is a relatively new non-contact deposition method that is highly suitable for organic based microelectronic fabrication owing to

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doi:10.1016/j.snb.2011.10.074

its micro-patterning capability, simple application procedure, low temperature processing and relatively low-cost instrumentation. Recently, inexpensive and disposable chemical/biosensors fabricated by inkjet printing have been demonstrated [18,19].

In this work, an electrochemically synthesized graphene-PEDOT:PSS (GP-PEDOT:PSS) is employed for the first time to modify screen printed carbon paste electrode (SPCE) by inkjet-printing technique. The inkjet-printed GP-PEDOT:PSS electrode is then applied for electrochemical detection of salbutamol by cyclic voltammetry (CV) and its performances are compared to PEDOT:PSS modified and unmodified SPCE. Salbutamol or [2-(tert-butylamino)-1-(4-hydroxy-3-hyroxymethyl) phenylethanol] is of interest because it is the most widely used β_2-adrenergic receptor agonist for curing bronchial asthma and other allergic diseases [20,21] while it is also a banned drug for athletes and a prohibited food additive. Due to its importance, electrochemical detections of salbutamol have been widely investigated as an alternative determination method to standard analysis techniques including mass spectrometry [22,23] and UV–vis spectroscopy [24]. Over the past decade, electrochemical detections of salbutamol by glassy carbon [25], carbon paste [26], boron-doped diamond [27], CNTs [28,29] and graphite nanosheet modified electrodes [30] have been presented. However, there has been no report of its electrochemical detection by a GP-PEDOT:PSS modified electrode.

2. Materials and methods

2.1. Materials and apparatus

All of chemicals used in this work were analytical grade. Standard solutions of salbutamol were purchased from Sigma (USA). Phosphate buffer solution (pH 5.8–8.0) was made from sodium dihydrogen phosphate (Fluka, Switzerland) and disodium hydrogen phosphate (Fluka). The stock solution of salbutamol (0.01 mol l^{-1}) was prepared by dissolving 0.03 g of salbutamol in deionized distilled water. Graphite rods (1/4″ dia, Electron Microscopy Science) were used as starting material for graphene synthesis. A commercial PEDOT:PSS solution (clevios P jet N from HC Starck, USA) was utilized as an electrolyte for electrolytic exfoliation. SPCE electrodes were fabricated in-house at King Mongkut University of Technology at Thonburi, Thailand. An inkjet printer (Fujifilm Dimatix Materials Printer) was employed for printing of GP-PEDOT:PSS layers on SPCEs. A potentiostat (μ-autolab Type III, Metrohm, Switzerland) and a home-made electrochemical cell comprising a 3 ml cylindrical acrylic cell, a GP-PEDOT:PSS working electrode, a platinum (Pt) wire counter electrode and a silver/silver chloride (Ag/AgCl) reference electrode were used for all CV measurements.

2.2. Graphene synthesis

Two graphite rods were placed in an electrolysis cell filled with PEDOT:PSS electrolyte and a constant potential of 8 V was applied between electrodes using Keithley 2420 Source Meter. The anode was corroding and black precipitate was gradually formed in the reactor. The electrolysis was conducted for 5 h to obtain stable GP-PEDOT:PSS dispersion with a suitable graphene concentration. The dispersed product was centrifuged at 1200 rpm to separate large agglomerates and supernatant portion of the dispersion was decanted. The morphology and structure of graphene dispersed in the solution were characterized by transmission electron microscope (JEOL model JEM-2010) and confocal Raman spectroscope (NT-MDT model Ntegra Spectra). TEM samples were prepared by drop-coating of graphene-PEDOT/PSS solution on a carbon/copper grid while Raman and FTIR samples were washed graphene and unwashed graphene-PEDOT/PSS powders extracted from the solution.

2.3. Inkjet printing of GP-PEDOT:PSS electrodes

The GP-PEDOT:PSS solution was used as an ink for inkjet printing. The ink was loaded into a cartridge and printed on SPCE by the commercial material inkjet printer. One to five layers of GP-PEDOT:PSS material were printed on SPCE over an area of 3 mm × 5 mm. The surface morphology and functional group of GP-PEDOT:PSS printed films were characterized by scanning electron microscope (SEM, Hitachi model S-4700) and Fourier transform infrared spectroscopy (FTIR, Perkin Elmer model spectrum spot light-300), respectively.

2.4. Electrochemical measurement

The electrochemical characteristics of inkjet-printed GP-PEDOT:PSS modified SPCEs were measured by CV using the commercial electrochemical work station and home-made electrochemical cell. Salbutamol solutions with different concentrations

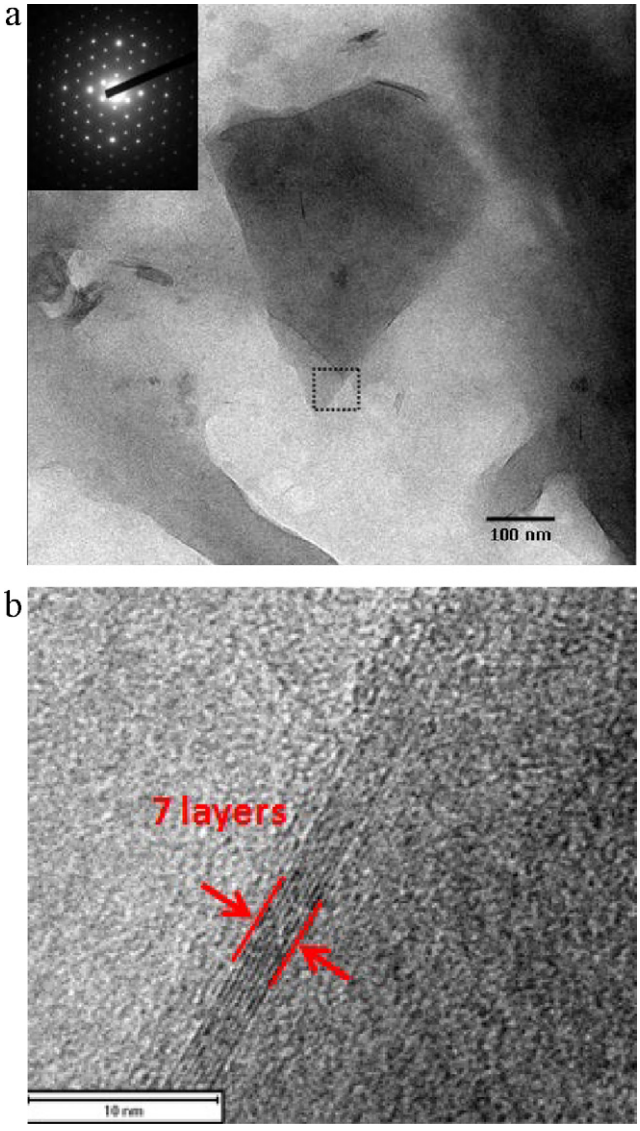

Fig. 1. (a) Bright field TEM image and (b) high-resolution TEM images of graphene sheet in GP-PEDOT:PSS composite. Inset: selected area electron diffraction pattern of a region near an edge of graphene sheet.