



Polythiophene/graphene oxide nanostructured electrodeposited coating for on-line electrochemically controlled in-tube solid-phase microextraction



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ABSTRACT

In this work, a novel polythiophene/graphene oxide (PTh/GO) nanostructured coating was introduced for on-line electrochemically-controlled in-tube solid phase microextraction of amitriptyline (AMI) and doxepin (DOX) as antidepressant drugs. The PTh/GO coating was prepared on the inner surface of a stainless steel tube by a facile in-situ electro-deposition method and it was used as a working electrode for electrochemically control in-tube solid phase microextraction. In the PTh/GO coating, GO acts as an anion dopant and sorbent. The PTh/GO coating, compared to PTh and GO coatings, exhibited enhanced long lifetime, good mechanical stability and a large specific surface area. Regarding the in-tube SPME, some important factors such as the extraction and desorption voltage, extraction and desorption times and flow rates of the sample solution and eluent, which could affect the extraction and separation efficiency of the analytes, were optimized. Total analysis time of this method including the online extraction and desorption time was about 21 min for each sample. AMI and DOX were extracted, separated and determined with limits of detection as small as $0.3 \mu\text{g L}^{-1}$ and $0.5 \mu\text{g L}^{-1}$, respectively. This method showed good linearity in the range of $0.7\text{--}200 \mu\text{g L}^{-1}$, $2.3\text{--}200 \mu\text{g L}^{-1}$ and $2.9\text{--}200 \mu\text{g L}^{-1}$ for AMI, and in the range $0.9\text{--}200 \mu\text{g L}^{-1}$, $2.5\text{--}200 \mu\text{g L}^{-1}$ and $3.0\text{--}200 \mu\text{g L}^{-1}$ for DOX in water, urine and plasma samples, respectively; the coefficients of determination were also equal to or higher than 0.9976. The inter- and intra-assay precisions (RSD%, $n=3$) were in the range of 2.8–3.4% and 2.9–3.9% at the three concentration levels of 5, 25 and $50 \mu\text{g L}^{-1}$, respectively. Finally, under the optimal conditions, the method was applied for the analysis of the drugs in human urine and plasma pretreated samples and good results were obtained.

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1. Introduction

Solid phase microextraction, which integrates concentration, extraction and sample introduction in to a single step, was first introduced by Pawliszyn and et al. [1]. Afterwards, diverse methods of SPME based on coated fibers, stirrers, vessels and membranes were developed [2,3]. To further enhance the extraction capacity and improve the stability of the fiber in SPME methods, in-tube solid-phase microextraction (IT-SPME) as a form of capillary microextraction (CME) was developed in 1997 [4]. Since the length and surface area of the coating in IT-SPME method is much higher than that used in fiber SPME, this method can provide greater extracting phase loading, increase sample capacity and improve

extraction sensitivity. In addition, IT-SPME offers easy automation of the extraction process by on-line coupling to HPLC.

Generally, the majority of the accessible IT-SPMEs use an open tubular fused-silica capillary with an inner surface coating [5,6]. These IT-SPME capillaries are limited to some applications considering their low mechanical stability and easy swelling in organic solvents, which may lead to fiber breakage and loss of coatings, which, in turn, can largely affect the extraction efficiency and lifetime [7]. Therefore, it is necessary to develop new coating materials for IT-SPME to extend its application in this area. So far, in the IT-SPME method synthesis, a lot of coatings have been reported to increase the extraction efficiency of different analytes [8,9].

Up to the present time, many methods including sol-gel [10,11], chemical bonding [12,13], physical deposition [14] and electrodeposition [15] have been developed in order to prepare IT-SPME coatings. Among these methods, electro-deposition method is simple, iterative, rapid, and the film thickness can be easily controlled [16]. However, IT-SPME method has shown poor selectivity and low

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extraction efficiency with regard to ionic compounds [15,17,18]. To overcome this problem, recently, an in-tube SPME method has been developed for the determination of ionic compounds by coupling the methods with electrochemically-controlled extraction, or IT-SPME (EC-IT-SPME) method [9,15]. So, in this method, similar to IT-SPME method, the selection of a suitable adsorbent is necessary.

In recent years, there has been an increasing interest in conducting polymers because of their various applications. A conducting polymer is especially promising for extraction applications because of its good mechanical stability, facile synthesis and higher conductivity. These polymers provide different intermolecular interactions such as acid-base, π - π , dipole-dipole, hydrophobic, and hydrogen bonding, with different analytes. Also, they have ion exchange properties. Polythiophene (PTh), one of the most important materials in the family of the conducting polymers, has attracted intense interest due to its promising electric, electrochemical and optical properties [19].

On the other hand, carbon-based nanomaterials have attracted the greatest interest in many fields, including analytical chemistry, due to their huge surface area, remarkable electronic properties and excellent mechanical, electrical and chemical properties. Graphene oxide (GO), as a new member of the carbon family, has been employed as an adsorbent for the SPME fiber [20] because GO contains a range of surface O-functionalities such as carboxyl, carbonyl, hydroxyl, and phenol groups [21]. In addition, its large delocalized π -electron system also endows GO with a strong affinity for carbon-based ring structures, which are prevalent in drugs, pollutants, and biomolecules [22]. Due to the poor conductivity of GO, conducting polymers are suitable candidates to combine with GO to form a novel conducting composite for various applications [23].

Previous studies indicated that the use of composite materials in SPME and IT-SPME methods are essential to improve the electrical, selectivity, effective surface area, porosity and mechanical properties of coatings [24,25], and composite polymers compared with conventional polymers, often exhibit remarkable improvements in the properties of material. In continuing our previous studies on developing EC-IT-SPME method [9,15], a new nanostructured coating consisting of PTh doped with GO was synthesized on the internal surface of a stainless-steel tube by a facile in-situ electro-deposition method. Then, it was utilized for on-line EC-IT-SPME coupled with HPLC-UV for the determination of antidepressant drugs 'amitriptyline (AMI)' and 'doxepin (DOX)' as model analytes in pretreated biological samples.

2. Experimental

2.1. Chemicals and reagents

All chemicals were of analytical reagent grade. AMI ($pK_a = 9.40$, >99% pure), DOX ($pK_a = 9.76$, >99% pure), synthetic thiophene (98% pure) and NaClO_4 (98% pure) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). The stock solutions of the AMI and DOX (1000 mg L^{-1}) were prepared by dissolving 10 mg of the compounds in 10 mL methanol and lower concentrations were prepared by diluting the stock solution with methanol. Methanol, acetonitrile, sodium hydroxide and hydrochloric acid (95% pure), graphite powder (50 mesh), H_2SO_4 (95%), NaNO_3 (95% pure), KMnO_4 (99% pure) and H_2O_2 (35% pure) were purchased from Merck (Darmstadt, Germany). Ultra-pure water was produced using a Youngling ultrapure water purification system model Aqua MaxTM-ultra (Seoul, South Korea). Other applied chemicals were of analytical reagent grade or of the highest purity available.

2.2. Apparatus

The chromatographic analysis was performed with a HPLC instrument including a Varian 9012 HPLC pump (Walnut Creek, CA, USA), a six-port Cheminert HPLC valve from Valco (Houston, TX, USA) with a 20- μL sample loop and equipped with a Varian 9050 UV-vis detector (Walnut Creek, CA, USA). The separations were run on an ODS-3 column (250 mm \times 4.6 mm, with a 5- μm particle size) from Hector Company (Daejeon, Korea). The mobile phase consisted of 10 mmol L^{-1} phosphate buffer, pH 4.0, and acetonitrile (57:43 V/V). The flow rate of the mobile phase was set at 1.0 mL min^{-1} . The total analysis time was 15 min and detection was performed at the wavelength of 210 nm. The chromatographic data were recorded and analyzed using Chromana software (version 3.6.4). GPFA1-380 peristaltic pump from Ultra-Voltammetry Company (Tehran, Iran) was applied to pass the solutions through the stainless-steel capillary tube. All the pH measurements were performed with a WTW Inolab pH meter (Weilheim, Germany). A potentiostat and galvanostat Auto lab system with PGSTAT30 and GPES 4.9 software from Eco Chemie (Utrecht, the Netherlands) were used for the electrochemical preparation of the coatings. IR spectra were obtained on an IFS 66 v/s IR spectrometer (Bruker, Germany). The particle size and morphology of the synthesized nanoparticles (NPs) were determined by a scanning electron microscope (SEM) model EM3200 from KYKY Zhongguancun (Beijing, China).

2.3. Preparation of polymer-coated capillary tubes and techniques to characterize coating

The GO was synthesized from natural graphite powder based on a modified Hummers method [26]. Then, GO (50 mg) and thiophene (0.8 mmol or 640 μL) were dispersed in 40 mL acetonitrile and sonicated for 90 min. Before electrochemical deposition, the steel tubes were cleaned by acetone and HPLC-grade water and finally air-dried at the room temperature. After that, the GO doped PTh film was generated on the inner surface of the stainless steel tube by applying a constant potential of +3.0 V for 30 min. During the electropolymerization, a dark film slowly formed on the inner surface of the stainless steel tube. The schematic representation of the electropolymerization of PTh-GO in the inner surface of the tube is shown in Fig. 1. A stainless steel tube (10 cm in length and 0.75 mm in diameter) was employed as the working electrode; Platinum and saturated Ag/AgCl electrodes were used as the counter and reference electrodes, respectively. A peristaltic pump was used to deliver the monomer solution through the inner surface of the stainless steel tube. After electrochemical deposition, the steel tube coated with PTh-GO film was washed with methanol, acetone, and water in sequence, and dried under nitrogen gas flow. After preparing the sorbent, the PTh, GO and PTh/GO coatings were characterized by Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). To take the SEM image from the inside of steel tube, a part of the tube was carefully cut with a coping saw and the SEM image was taken.

To verify the mechanical stability, inflation, acid and alkaline resistance of the present coating, methanol, acetonitrile, acetone, hydrochloric acid (1 mol L^{-1}) and sodium hydroxide (1 mol L^{-1}) were directly passed through the coated capillary for more than 10 h. Finally, the PTh/GO coated capillary was used to extract the AMI and DOX. The tube to tube repeatability was controlled by calculating the relative standard deviation (RSD%) for the extraction of AMI and DOX extraction by using three repetitions under the same conditions.

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