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Polydopamine-sheathed electrospun nanofiber as adsorbent for determination of aldehydes metabolites in human urine

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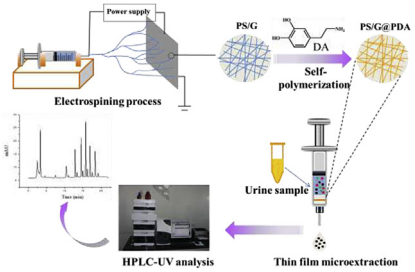
HIGHLIGHTS

- An electrospun PS/G@PDA nanofiber membrane was fabricated for thin film microextraction.
- The membrane exhibited satisfactory hydrophilicity, large surface area, high extraction efficiency and special selectivity.
- A fast, convenient, sensitive, high-efficient and matrix-free method was developed.
- The method was applied for the determination of urinary aldehyde metabolites.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, a novel polydopamine modified polystyrene/graphene electrospun nanofiber membrane (PS/G@PDA) was fabricated on the surface of filter paper and used for thin film microextraction (TFME) for the first time. Benefiting from the hydrophilic polydopamine (PDA) coating and the porous fibrous structure, the PS/G@PDA membrane exhibited large surface area, high extraction efficiency, rapid extraction equilibrium, special selectivity and excellent biocompatibility. A thin film microextraction-high performance liquid chromatography method was developed and applied for the analysis of six aldehyde metabolites in human urine samples. Under the optimal conditions, the recoveries of the aldehyde compounds varied in the range of 83%–115%, with the relative standard deviation values lower than 14.5% (n = 5). Moreover, satisfactory sensitivities with the limits of detection in the range of 2.3–6.5 nmol L^{-1} and good linearity with excellent correlation coefficients (R^2) being larger than 0.9936 had also been achieved. In general, a fast, convenient, sensitive, high-efficient and matrix-free method was successfully proposed and expected becoming a promising approach for the determination of trace aldehyde metabolites in complex biological samples.

1. Introduction

Thin-film microextraction (TFME), a novel solid phase microextraction technique, was introduced by Pawliszyn and co-workers [1]. In this microextraction approach, a sheet of flat film with large volume and high surface area-to-volume ratio is used as the extraction phase, short equilibration times, great extraction rates,

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high extraction efficiency and sensitivity are the attractive features of the method [2,3]. Due to the excellent performance of this method, TFME has gained widely applications for trace analysis in food [4], drug [5], environmental [6] and biomedical fields [7] in recent years. For example, Saraji et al. developed a chemically modified cellulose paper as a thin film microextraction phase which was applied for the determination of estrogenic hormones in environmental water and positive results were obtained [8]. Besides, a new poly (vinylidene fluoride) membrane-based TFME method was also developed for the extraction of benzoylurea insecticides from water samples followed by HPLC analysis [9].

There were different ways to fabricate the thin film extraction phase for TFME. So far, the reported methods include spraying [10], spreading [11], dipping [12] and electrospinning [13]. Of which, electrospinning has been reported as a versatile, flexible and promising method to prepare non-woven mats of polymer nanofibers and has obtained tremendous attention in last decade [14]. The diameter, morphology, and orientation of the nanofiber can be accurately controlled through adjustment of the polymer solution and the setup [15]. Thanks to the large surface area-to-volume ratio, high porosity and degree of interconnection of the nanofibers, the as-spun fibers have been applied in many fields, such as filtration, biomedical application, and wastewater treatment [16]. Besides, the electrospinning technique has already been introduced to prepare thin film extraction materials as the spun nanofiber can be uniformly deposited on a flat substrate forming thin film [13]. For example, Guan et al. prepared an acetone-activated polyimide electrospun nanofiber membrane to extract phenols in environmental water [17]. Currently, various hybrid nanofibers have also been fabricated through doping organic or inorganic material into the electrospun polymer solution [18,19]. Graphene, as a charming two-dimensional carbon material, has ultrahigh surface area-to-volume ratio, excellent mechanical, electrical and thermal performances. With the doping of graphene, the composite nanofiber exhibited larger surface area-to-volume ratio, enhanced mechanical and physical properties [20,21] and super hydrophobicity [22]. However, the strong hydrophobicity of the nanocomposite fibers is not benefit for the sufficient contact of the inner surface of nanofiber with the aqueous solution, which possibly results in the limited extraction efficiency. And it has been proved that a hydrophilic surface can effectively resist biofouling by forming a thin water layer on it [23,33,34]. Therefore, hydrophilic surface modification of the extraction phase is vital for bioanalysis, especially for trace bioanalysis.

Polydopamine (PDA), a mussel-inspired polymer, was confirmed to have the ability of self-coating on an extensive range of materials in the presence of oxygen by mild oxidative polymerization of dopamine under alkaline conditions [24]. The polydopamine coated materials possess unique features, such as good dispersibility in water, charming biocompatibility, easily secondary modifying (with abundant amino and catechol groups), and it can offer π-π stacking interaction with the analytes [25]. The PDA coated materials are regarded as a novel extraction medium in sample preparation [26], including SPE [27], SPME [28], even in vivo analysis [29,30]. For example, polydopamine modified nanofibers followed by cross-linking with glutaraldehyde (PS@PDA-GA) were prepared and used to determine pharmaceuticals in living fish muscle [23].

The objective of this research is to establish a hydrophilic polystyrene/graphene@polydopamine nanofiber membrane as the extraction phase of thin-film microextraction. The morphology, microstructure and resistance capacity to matrix effect of the membrane were investigated. Some experimental parameters affecting the derivatization and extraction efficiency were also studied systematically. Furthermore, analytical characteristics such as linearity, limit of detection, precision, and recovery were examined, and the developed method combined with high performance liquid chromatography was applied for the determination of aldehyde metabolites in urinary samples of lung cancer patients and healthy volunteers.

2. Experimental

2.1. Chemicals and materials

Butanal (98%) and octanal (98%) were purchased from TCI Development Co. LTD. (Shanghai, China). Heptanal (97%) was supplied by ABCR GmbH & Co. KG (Germany). Pentanal (98.5%) was bought from Amethyst Chemicals (Beijing, China). Hexanal (97%) and dopamine hydrochloride (98%) were obtained from Aladdin Industrial Corporation (Shanghai, China). Nonanal was obtained from Alfa Aesar (Tianjin, China). Formic acid (99%) was supplied by Tedia (USA). 2, 4-Dinitrophenylhydrazine (DNPH, 98%) was provided by J&K Chemical Corporation (Beijing, China) and recrystallized once in acetonitrile-water (1:5) solution before use. HPLC-grade methanol was acquired from Tedia Company (Fairfield, OH, USA), and filtered by microporous filter membrane (0.45 μm). HPLC-grade ethanol, isopropanol, and acetonitrile were obtained from Merck (Darmstadt, Germany). Polystyrene (PS, average MW ~ 192,000) was purchased from Sigma-Aldrich (USA). Dimethyl formamide (DMF) and sodium chloride were acquired from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Graphene was obtained from Xfnano (Nanjing, China). Bovine serum albumin (BSA) and Tris(hydroxylmethyl)methylaminomethane (Tris) were obtained from Ruji Biotech. Co. (Shanghai, China). β-Glucuronidase/arylsulfatase was supplied by Merck (Germany) and other chemical reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultra-pure water was used in all experiments (arium® pro Ultrapure Water Systems, Sartorius Stedim Biotech, Gottingen, Germany).

2.2. Chromatographic apparatus and operating condition

The Agilent 1100 series HPLC system (Agilent Technologies, PaloAlto, CA, USA) equipped with a variable wave-length detector which set at 360 nm was used in this study. The analytes were separated on an Eclipse XDB-C18 column (250 mm × 4.6 mm, 5 μm, Agilent Technologies Inc., USA). The mobile phase was composed of methanol (mobile A) and water (mobile B) at a flow rate of 1.0 mL min^{-1} (40 °C) and the injection volume was 10 μL. The linear gradient elution was as follows: 0–6 min, 75% A; 6–12 min, 75–93% A; 12–18 min, 93% A; 18–25 min, 93%–75% A; 25–27 min, 75% A.

Surface morphology of the nanofiber membrane was photographed by scanning electron microscope (SEM, JSM-IT300, Japan) and transmission electron microscope (JEOL, JEM-2100 (HR), Japan). The specific surface area was measured using the Brunauer-Emmett-Teller method (BEL SORP-mini BEL Japan Inc., Japan) by nitrogen adsorption/desorption. Before the BET testing, the sample was under nitrogen (N_2) at 60 °C for 2 h to outgas. Contact angles of the nanofiber membrane for water were determined by OCA20 contact angle meter (Dataphysics, Germany).

2.3. Preparation of standard solutions

The stock solution containing six aldehydes (butanal, pentanal, hexanal, heptanal, octanal and nonanal) was prepared in methanol at each concentration of 500 μmol L^{-1} and stored at −20 °C. All the daily standard working solutions were prepared by appropriate dilution of the stock solution with ultra-pure water as need.