Incorporation of carbon nanotubes into graphene for highly efficient solid-phase microextraction of benzene homologues

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ABSTRACT

3D graphene-carbon nanotubes (G-CNTs) composite with unique morphology and structure was prepared by one-step insertion of CNTs into graphene. Subsequently, the G-CNTs composite as a fiber coating material for solid-phase microextraction (SPME) was fabricated on the surface of a stainless steel wire by direct coating method. The prepared coating was tested by the extraction of benzene homologues (BTEX, benzene, toluene, ethylbenzene and m-xylene). Compared with a commercial polydimethylsiloxane (PDMS) fiber, the home-made coating exhibited higher extraction performance for BTEX, and the reasons were discussed systematically. Under the optimized conditions, the prepared coating coupled with chromatography-mass spectrometry (GC–MS) for the analysis of BTEX exhibited wide linear ranges, low limits of detection (3 S/N) (LODs, 0.59–2.68 ng L^{-1}), low limits of quantification (10 S/N) (LOQs, 1.96–8.92 ng L^{-1}), good repeatability (3.2–5.5%, n = 6) and reproducibility (3.7–9.1%, n = 3). Finally, the developed method was successfully applied to the analysis of BTEX in environmental water samples with satisfactory recoveries (84.7–108.1%). This study is expected to further the exploration of high-performance SPME coating materials, and broaden the applications of graphene-based materials.

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1. Introduction

Solid-phase microextraction (SPME) is a simple, green and equilibrium-based sample pretreatment technique [1]. Since its introduction, SPME has made great advances in analytical fields, such as environmental monitoring [2,3], food safety [4–6], forensic toxicology [7], pharmaceuticals and biological analysis [8–10]. The development of new SPME fibers is contemporarily one of the hottest research topics in SPME technique, owing to the fact that it is based on the distribution of analytes between sample matrixes and the coating. The sensitivity, selectivity and mass transfer rate of this technique are determined by the properties of the coating materials, which possess adsorption affinity towards the analytes through covalent bonds, non-covalent interactions and pore structures [11–13]. To date, because the types of the commercially available SPME fibers are limited, novel materials of various structures and morphologies, including polymers [14], metal organic frameworks (MOFs) [15], carbon materials [16], silica [17], and metal oxides [18], have been synthesized and utilized as SPME fiber

coatings with excellent thermal stability, chemical stability, mechanical stability and greatly enhanced extraction performance for analytes of interest [19–25].

Graphene has been developed as a SPME fiber coating owing to its remarkable thermal stability, chemical stability and good affinity towards many aromatic compounds [22,26,27]. In addition, the composites of graphene with other materials through covalent modification, non-covalent decoration and doping can also effectively improve the extraction performances of SPME fiber coatings [28–31]. For example, the amino-functionalized graphene coating exhibited higher extraction efficiency to five synthetic musk than a non-functionalized one, because the introduction of -NH$_2$ into graphene can avoid agglomeration, and provide more non-covalent binding sites for the target analytes [29]. A nitrogen-doped graphene coating showed excellent adsorption capability for six polycyclic aromatic hydrocarbons (PAHs) by forming strong hydrophobic and π-stacking interaction between the coating and the analytes [30]. A ZnO/graphene composite coating showed higher extraction selectivity and sensitivity towards 1-octanethiol, which was attributed to an outstanding synergistic effect between the large specific surface area of graphene and the high affinity of ZnO to the mercapto groups [31]. Nevertheless, some of the potential characteristics of

graphene as adsorbent for SPME have not been explored. There is a way to tune its properties via conformation regulation, which would enhance the adsorption performance of graphene for SPME and other applications.

Carbon nanotubes (CNTs) are regarded as a type of rolled-up graphene. The introduction of CNTs within graphene is a great way to ameliorate the conformation of graphene and create a new desired 3D morphology with new adsorption sites. As a result, the extraction capacity of the home-made composite coating could be enhanced.

In this study, G-CNTs composites were prepared to fabricate SPME fiber coatings, and applied to the analysis of BTEX in environmental water samples.

2. Experimental

2.1. Materials

All chemicals were at least of analytical grade and without extra purification. Benzene (99.9%), ethylbenzene (99.8%), and L-ascorbic acid were purchased from Aladdin (Shanghai, China). Toluene (99.8%) and *m*-xylene (99.5%) were purchased from Alfa Aesar (Beijing, China). Cyclohexane, methanol and acetone were obtained from Guangzhou Chemical Regent Company (Guangzhou, China). Multi-wall Carbon nanotubes were obtained from Chengdu Alpha Nano Technology Co., Ltd. (Sichuan, China). Neutral silicone sealant was offered by Sikasil Ltd. (Guangzhou, China).

The stainless steel wires (SSWs) (o.d. 127 μm) were obtained from Component Supply Company (Fort Meade, MD, USA). The commercial SPME fiber (30 μm PDMS) was obtained from Supelco (Bellefonte, PA, USA).

2.2. Apparatus

Micrographs of the samples were recorded by a Field Emission Scanning Eletron Microscope (FESEM, JSM-6330P, Japan). Nitrogen-adsorption isotherms were obtained by a Micromeritics ASAP 2020 V3.04H surface and porosity analyzer at 77 K. The microstructures of the samples were obtained by Fourier Transform Infra-Red Spectrometer coupled with infra-red microscope (FT-IR, EQUINOX 55, Germany), powder X-ray diffractometer (PXRD, D-MAX 2200 VPC, Japan), laser micro-Raman spectrometer with an excitation laser of 514 nm (Raman, Reniashaw inVia, UK). An Agilent 6890–5975 GC–MS system equipped with a HP-5 MS capillary column (30 m × 0.32 mm i.d. × 0.25 μm film thickness) (Palo Alto, CA, USA) was used for the analysis and quantification of BTEX. The evaluations of the SPME coatings towards BTEX were performed on an Agilent 7890 GC-FID (Palo Alto, CA, USA).

2.3. Preparation of the G-CNTs composites

Graphene oxide was synthesized via a modified Hummers method, and details of the preparation process were described in our work [32]. The G-CNTs composites were obtained by a mild one-pot hydrothermal process. In brief, 100 mL of graphene oxide homogeneous dispersion (2 mg mL^{-1}) and a given mass of CNTs (the weight ratio of graphene oxide to CNTs was varied as 10:1, 5:1, 2:1, 1:1, 1:2, and the composites were denoted as G-CNTs-10-1, G-CNTs-5-1, G-CNTs-2-1, G-CNTs-1-1, G-CNTs-1-2, respectively) were mixed by ultrasonication for 60 min. Then, 0.4 g of L-ascorbic acid was added into the above mixture and ultrasonicated for another 15 min. Finally, the mixture was transferred to a Teflon-lined autoclave and heated at 100 °C for 6 h.
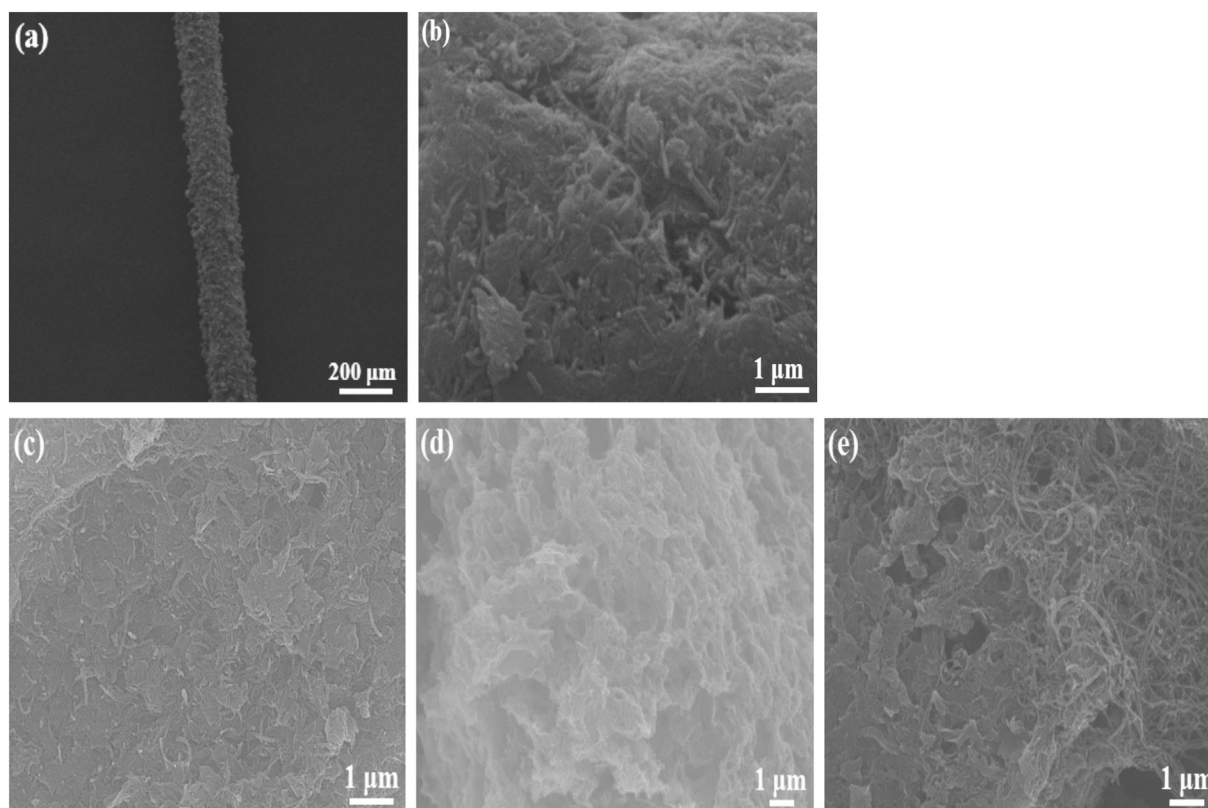

Fig. 1. Low magnification SEM image at 39 × of G-CNTs-5-1 coating (b), high magnification SEM image at 15000 × of G-CNTs-5-1 coating (c), SEM images of G-CNTs-5-1 powder (d), graphene powder (d), and G + CNTs-5-1 powder (e).