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Short Communication

New graphene fiber coating for volatile organic compounds analysis

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ABSTRACT

In the work, a novel graphene-based solid phase microextraction-gas chromatography/mass spectrometry method was developed for the analysis of trace amount of volatile organic compounds in human exhaled breath vapor. The graphene fiber coating was prepared by a one-step hydrothermal reduction reaction. The fiber with porous and wrinkled structure exhibited excellent extraction efficiency toward eight studied volatile organic compounds (two n-alkanes, five n-aldehydes and one aromatic compound). Meanwhile, remarkable thermal and mechanical stability, long lifespan and low cost were also obtained for the fiber. Under the optimal conditions, the developed method provided low limits of detection (1.0–4.5 ng L^{-1}), satisfactory reproducibility (3.8–13.8%) and acceptable recoveries (93–122%). The method was applied successfully to the analysis of breath samples of lung cancer patients and healthy individuals. The unique advantage of this approach includes simple setup, non-invasive analysis, cost-efficient and sufficient sensitivity. The proposed method supply us a new possibility to monitor volatile organic compounds in human exhaled breath samples.

1. Introduction

Recently, exhaled breath analysis has been considered to be a new approach to recognize lung cancer and infectious diseases in early stage [1,2]. The measurement of metabolites in human exhaled breath vapor (EBV) represents a non-invasive diagnostic approach through assessing volatile organic compounds (VOCs) generated in the organism. Due to its unique advantages: non-invasive, painless, inexpensive and easily accessible to a large number of patients, breath analysis has attracted a considerable amount of scientific and clinical interest, and significant progress has been obtained [1–3]. However, some main problems still challenge the existing analytical method of EBV. The low concentrations of VOCs in exhaled breath (nmol L^{-1} to pmol L^{-1}) may beyond instrument limits of detection [2], the co-existed compounds (nitrogen, oxygen, carbon dioxide, water and inert gases) in EBV lead to possible matrix interference. Therefore, for EBV analysis, sample preconcentration is greatly necessary before the quantitative analysis by gas chromatography/mass spectrometry (GC–MS) [4].

SPME has been known to be a versatile method for detection of volatile compounds in breath and blood [5]. It is attractive owing to its solvent-free, simplicity and rapidity. The most commonly applied fiber coatings are carboxen/polydimethylsiloxane (CAR/PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), polydimethylsiloxane (PDMS) and polyacrylate (PA). Due to the physical properties of the available fibers, the number of substances that can be adsorbed is limited [2].

In the past few years, many researchers contribute to the discovery and application of novel materials as SPME fiber coating for analytical sample preparation [6]. Graphene is considered to be one of the most promising carbon-based nanomaterials due to its unique two-dimensional planar monolayer structure, superior mechanical strength, remarkable thermal and chemical stability, ultrahigh specific surface area and hydrophobic property. These excellent features make graphene suitable as a good candidate of sorbents or fiber coating, and the relevant review about the application of graphene in sample preparation has been reported recently [7,8]. To the best of our knowledge, the majority of graphene-based SPME fibers were used in environmental analysis, it has not been used in the complex biological samples such as human exhaled breath.

The aim of the article is intended to develop a novel graphene fiber coating and evaluate its application in VOCs analysis. In our work, graphene fiber coating was prepared by a facile one-step hydrothermal reduction strategy. The characteristic properties of the fiber including thermal and mechanical stability, extraction performance and lifespan were studied systematically. Based

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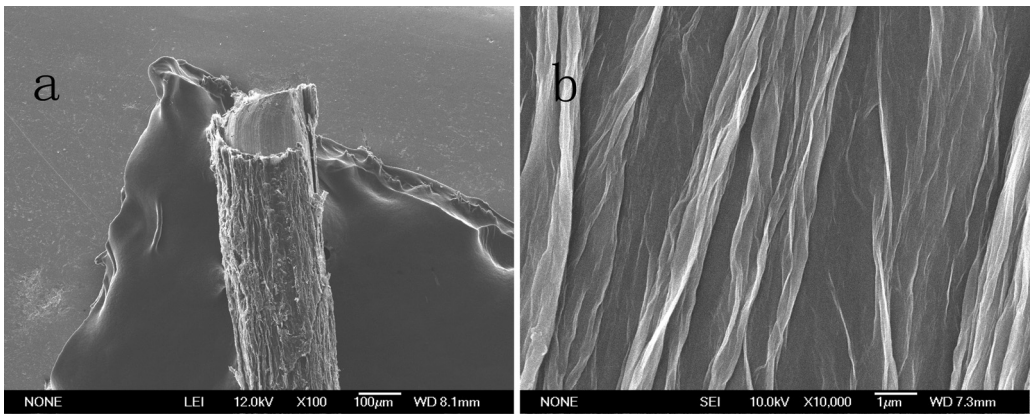

Fig. 1. Scanning electron microscope images of graphene fiber with magnification of 100× (a) and 10,000× (b).

on the fiber, a solid phase microextraction-gas chromatography/mass spectrometry (SPME-GC/MS) method was established for the enrichment of VOCs from human exhaled breath vapor. VOCs in exhaled breath such as aldehydes, alkanes and ethylbenzene were chosen as test analytes due to their potential disease diagnostic value for lung cancer [9–11]. VOCs studied in our work are listed in Table S1 of Supplementary contents. Experimental parameters that may influence the extraction and desorption were investigated. Under the optimal conditions, the proposed method was validated and applied in EBV analysis of healthy people and lung cancer patients. Comparison experiments with commercial fibers were also carried out.

2. Materials, instrumentation and methods

2.1. Chemicals, materials and instrumentation

The chemicals and materials used in the work, some parameters about the instrumentation are listed in Section 2 of Supplementary contents.

2.2. Standard solution and gas calibration sample

The preparation methods of standard solution and gas calibration samples of different concentrations are introduced in Section 3 of Supplementary contents.

2.3. Preparation of graphene fiber

A clean stainless steel wire with outside diameter of 0.2 mm was corroded with hydrofluoric acid (80 °C, 10 min) to generate a rough surface and used as support of graphene coating. Graphene fiber coating was prepared as described in Ref. [8] with minor modification. Briefly, graphene oxide (GO) suspension solution (2 mL water containing 50 mg GO) was injected into a glass capillary (length: 3.0 cm, i.d.: 1.0 mm). A corroded stainless steel wire with the same length (o.d.: 0.2 mm) was inserted into the capillary. Then the capillary was sealed and heated in stainless steel autoclave at 180 °C for 2 h. Finally, the graphene fiber was cooled and dried at 60 °C for 1 h.

2.4. SPME procedure

A graphene fiber with an effective length of 2 cm and a stainless steel wire (o.d.: 0.2 mm, length: 20 cm) were connected with a silica capillary (length: 5 mm, i.d.: 0.25 mm, o.d.: 0.32 mm) and fixed with epoxy glue. The long fiber was installed into a 5 μL microsyringe as SPME holder according to a previous literature [12]. Prior to the first usage, the graphene fiber was inserted into the GC injector and allowed to condition at 260 °C for 2 h. For VOC analysis, 2 μL of standard working solution was injected into a 20-mL evacuated sealed glass vial and evaporated in water bath (60 °C, 5 min). Then, the graphene fiber was exposed for extraction. After a certain time, the graphene fiber was withdrawn back into the syringe and immediately inserted into GC injector for thermal desorption at 260 °C for 6 min.

2.5. Sample collection

Five EBV samples of lung cancer patients and six samples of healthy volunteers were collected from Hubei Cancer Hospital, Hubei, China and Central China Normal University, separately. Each subject was asked to cleanse his (or her) mouth with water before sampling. Samples were collected into 1 L Tedlar® bags. Before sampling, the Tedlar bags were cleaned by flushing with ultra-clean nitrogen. Twenty milliliter exhaled air were transferred to an evacuated sealed 20-mL headspace vial by gastight syringe. All breath gas samples were processed within 3 h after sampling, and all measurements were made in duplicate.

3. Results and discussion

3.1. Characterization of materials

In this work, the graphene fiber was fabricated from GO suspensions by a facile one-step hydrothermal reduction strategy. SEM images (Fig. 1a and b) show that a graphene coating with the thickness of about 8 μm has been coated on the surface of the stainless steel wire, and the diameter of the graphene fiber is about 230 μm. Fig. 1b displays that a uniform, porous, wrinkled structure of graphene coating has been formed. The formation mechanism of the 3D cross-linking porous structure has been explained in a recent literature [7]. When GO sheets with 2D monolayer structure were hydrothermally reduced, they became regionally hydrophobic, the increased hydrophobicity and the π–π interactions led to a 3D random stacking between flexible graphene sheets.

3.2. Thermal stability of the fiber

Since thermal desorption at an elevated temperature was adopted in the work, the thermal stability of the coating was accessed by evaluating the performance of the fiber after it was conditioned for 40 min at 260, 280, 300 and 320 °C, successively. The experimental results showed that the extraction ability of the fiber was barely affected by the temperature change in the range 260–320 °C (Fig. S1, Supplementary contents). The observed results