



Preparation of sulfonated graphene/polypyrrole solid-phase microextraction coating by in situ electrochemical polymerization for analysis of trace terpenes[☆]



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ABSTRACT

In this study, a novel sulfonated graphene/polypyrrole (SG/PPy) solid-phase microextraction (SPME) coating was prepared and fabricated on a stainless-steel wire by a one-step in situ electrochemical polymerization method. Crucial preparation conditions were optimized as polymerization time of 15 min and SG doping amount of 1.5 mg/mL. SG/PPy coating showed excellent thermal stability and mechanical durability with a long lifespan of more than 200 stable replicate extractions. SG/PPy coating demonstrated higher extraction selectivity and capacity to volatile terpenes than commonly-used commercial coatings. Finally, SG/PPy coating was practically applied for the analysis of volatile components from star anise and fennel samples. The majority of volatile components identified were terpenes, which suggested the ultra-high extraction selectivity of SG/PPy coating to terpenes during real analytical projects. Four typical volatile terpenes were further quantified to be 0.2–27.4 $\mu\text{g/g}$ from star anise samples with good recoveries of 76.4–97.8% and 0.1–1.6 $\mu\text{g/g}$ from fennel samples with good recoveries of 80.0–93.1%, respectively.

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1. Introduction

Graphene (G) is a new class of carbon material with excellent thermal and chemical stability [1,2], ultra-high specific surface area and π - π electrostatic stacking property [3,4]. Recently, G-based enrichment media in sample preparation techniques have already been developed and actually applied for the analysis of pyrethroid pesticides [5], polycyclic aromatic hydrocarbons (PAHs) [6], organochlorine pesticides (OCPs) [7–9] and polybrominated diphenyl ethers (PBDEs) [10] and so on. Many attractive properties of G-based enrichment media such as extremely large surface area are associated with monolayer graphene sheets. However, pure G-based enrichment media easily tend to curl, corrugate and irreversibly agglomerate, which would result in its wrinkled structure not ever an atomically flat layer [3]. Therefore, the development of functionalized G composites-based enrichment media would facilitate the improvement of dispersibility and extraction selectivity,

which would further extend its application fields in analytical chemistry.

Functionalized G-based sampling techniques such as graphene oxide-bound-silica (GO@silica) and G-bound-silica (G@silica) solid phase extraction (SPE) [11], sulfonated graphene (SG) μ -SPE [12], G-Fe₃O₄ magnetic SPE [13,14], G-based metal oxide and polymer composite solid phase microextraction (SPME) [15,16], and polydopamine layer-by-layer assembled functional graphene oxide (FGO-PD) SPME [17] have been successfully developed for sample preparation. Especially, SG is one of the most attractive potential G-composite media, since p-phenyl-SO₃H groups are introduced in the mother structure of G [18], which would avoid aggregation and obtain monolayer G-based material with ultra-high specific surface area. Therefore, SG possesses higher extraction capacity, and the introduction of negatively charged -SO₃H groups in G will also improve its extraction selectivity for target analytes. Pure SG adsorbent materials have been applied for the analysis of persistent aromatic pollutants such as naphthalene and 1-naphthol [19,20] and PAHs [12] in water samples. These preliminary studies validated SG sheets possessed excellent extraction capability.

Due to the extremely high mobility and volatility of gas, it is hard to guarantee the efficiency and reproducibility of a gas sampling process. Thus, efficient enrichment techniques for volatile organic

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compounds (VOCs) still remain a challenge in analytical chemistry nowadays. Until now, sorbent tube [21], thin film microextraction [22] and SPME [23] have been employed as commonly-used VOC sampling techniques. Among them, SPME has been proved to be an excellent sampling technique for VOCs, since it is simple, miniaturized, rapid and environment-friendly with convenient sampling operation. Moreover, headspace SPME (HS-SPME) is very suitable for non-invasive monitoring of the original amounts of target volatiles from real samples, since a small fraction of free volatiles is extracted from samples during an SPME process, and negligible depletion extraction results in little disturbance to the system under study [24].

Star anise (*Illicium verum*) and Fennel (*Foeniculum vulgare*) are important traditional Chinese medicines as well as commonly-used spices for Chinese cuisines. Their flavor compositions contain many volatile terpenes which possess crucial pharmacological actions such as antimicrobial, antioxidant, anti-inflammatory, insecticidal, analgesic and anticancer activities [25,26]. Volatile terpenes are usually at trace content levels with strong volatility. Until now, there are still no proposed SPME coatings actually applied for selectively sampling trace terpenes from real spice samples, due to their poor adsorption affinity toward trace terpenes. Development of novel efficient and selective SPME coatings might finally conquer the difficulty in the precise analysis of trace terpenes from real spice samples.

Generally, preparation methods for G-based SPME coatings mainly include physical doping [5,7], coating adhesion [8], layer-by-layer chemical bonding [6,17], sol-gel technology [9,10,15,16,27], chemically coating techniques [28], and electrochemical polymerization method [29]. Compared with other preparation methods, electrochemical polymerization is a simple and flexible preparation method. SPME coating can be directly in situ fabricated on a metal wire substrate via a one-step electrochemical polymerization procedure. Moreover, electrochemical polymerization conditions such as applied potential and polymerization time can be easily controlled by a three-electrode system to achieve stable and reproducible SPME coatings [30]. As mentioned above, SG possesses high specific surface area and stable dispersibility. When SG is combined with conducting polymer of polypyrrole (PPy), negatively charged SG sheets will be easily dispersed in the acidic electrolyte and acted as dopants of PPy [31]. Via electrochemical polymerization SG/PPy SPME coating would be prepared and directly fabricated on the surface of stainless-steel wire. SG/PPy SPME coating is expected to possess excellent mechanical durability, thermal stability, extraction capacity and extraction selectivity for target analytes with conjugated structures due to the introduction of PPy which would further enhance the π - π conjugated interactions between conjugated targets and SG/PPy coating.

In this study, SG/PPy SPME coating was prepared directly on the stainless-steel wire by a simple in situ electrochemical polymerization method under optimal conditions. Extraction capacity and selectivity of this coating was investigated in detail. Finally, this novel SG/PPy SPME coating was actually applied for the selective analysis of trace terpenes from star anise and fennel samples coupled with gas chromatography/mass spectrometry (GC/MS) detection.

2. Experimental

2.1. Chemical reagents and materials

Stainless-steel wires (od, 0.20 mm) were supplied from Laiwu Longzhi Metal Yarn Factory (Shandong, China). Graphite powder (99.95%, particle size $\leq 30 \mu\text{m}$), sodium borohydride (98%) and

sulfanilic acid (>98%) were purchased from Alfa Aesar. Pyrrole (99%), dodecylbenzene sulfonic acid (DBSA, >99%), linalool (98%), dipentene (95%), camphene (95%), cineole (>99.5%), 1-nonanol (98%) and 1-decanol (98%) were purchased from Aladdin (Shanghai, China). γ -Terpinene (95%) was purchased from TCI (Tokyo, Japan). α -Pinene (97%) and 3-carene (90%) were purchased from J&K Chemical Ltd. (Beijing, China). 1-Butyl butyrate (99%), 1-amyl butyrate (99%), isoamyl isovalerate (98%) and 1-octanol (99%) were obtained from Aldrich (St. Louis, MO, USA). HPLC grade n-hexane was obtained from Fuchen Chemical Reagents (Tianjin, China). All other chemicals were analytical grade. The high-purity helium (99.999%) was purchased from Guangzhou Xicheng Gas Factory (Guangzhou, China).

The mixed standard stock solutions of seven terpenes for the study of extraction capacity were prepared by dissolving 10.0 μL of α -pinene, 3-carene, dipentene, cineole, γ -terpinene and linalool and 10.0 mg of camphene in 10.0 mL of n-hexane. The evaluation for the extraction selectivity of SG/PPy SPME coating was conducted based on the mixed standard solutions of terpenes, alcohols and esters which were prepared by dissolving 10.0 μL of three terpenes (γ -terpinene, dipentene and 3-carene), three alcohols (1-octanol, 1-nonanol and 1-decano) and three esters (1-amyl butyrate, 1-hexyl butyrate and isoamyl butyrate) in 10.0 mL of n-hexane. The daily working solutions were prepared by appropriate dilution with n-hexane and stored at 4 °C in brown glass bottles.

2.2. Instruments

An electrochemical workstation (Ingsens-1010, Ingsens instrument Co. LTD, GuangZhou) was used for the preparation of SG/PPy SPME coating. A 200 W entire intelligent ultrasonicator (KQ 5200, Kunshan, China) was used to achieve the dispersive SG and clean stainless-steel wires. HS-4 magnetic stirrer (IKA RET, Germany) was employed for stirring solutions. The morphological studies of SG/PPy SPME coating were characterized by a JSM-6330F (JEOL, Tokyo, Japan) scanning electron microscopy (SEM). NICOLET AVATAR 330 Fourier transform infrared spectrometer (FT-IR) was used to record IR spectra of this coating. The X-ray diffraction (XRD) was performed on a D8 Advance X-ray diffractometer with Cu $K\alpha$ incident radiation. The thermal stability of this coating was evaluated by a thermogravimetric (TG) analyzer (Netzsch-209, Bavaria, Germany). Commercial SPME coatings involving 100 μm polydimethylsiloxane (PDMS), 75 μm carbowax/polydimethylsiloxane (CAR/PDMS) and 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) coatings were obtained from Supelco (St. Louis, MO) for the comparison experiment.

An Agilent HP 6890 gas chromatography-5973 mass detector system (Palo Alto, CA, USA) equipped with an HP-VOC fused silica capillary column (60 m length \times 0.320 mm I.D. \times 1.80 μm film thickness) (Agilent Technologies, Palo Alto, CA, USA) was used in the study. Helium was used as carrier gas at a flow rate of 1.0 mL/min. The instrumental conditions were as follows: the injector temperature, 250 °C; splitless mode; transfer line temperature, 280 °C; energy of electron, 70 eV; ion source temperature, 230 °C; MS Quad, 150 °C. Terpenes VOCs were identified by scanning mode according to the standard mass spectra of the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) MS spectral library. VOCs were considered 'identified', when their mass spectral fit values were at the default value of 85 or above. For star anise VOCs, the GC/MS oven temperature programming was follows: initial 50–130 °C at a ramp rate of 10 °C/min, and then increased to 260 °C at a ramp rate of 4 °C/min. For fennel VOCs, the GC/MS oven temperature programming was follows: initial 50–110 °C at a ramp rate of 20 °C/min, and then increased to 210 °C at a ramp rate of 4 °C/min. The oven temperature for the study of extraction capacity

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