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Doping of three-dimensional porous carbon nanotube-graphene-ionic liquid composite into polyaniline for the headspace solid-phase microextraction and gas chromatography determination of alcohols

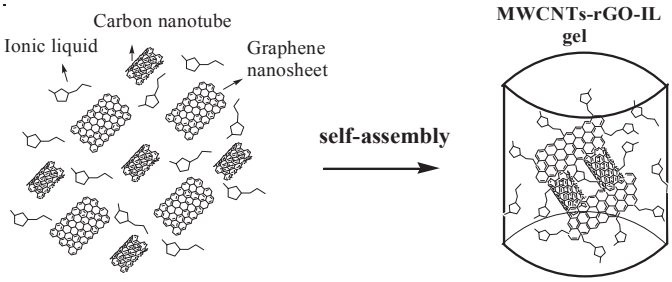
Lulu Li, Mian Wu, Yingying Feng, Faqiong Zhao, Baizhao Zeng*

Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, 430072, Hubei Province, PR China

HIGHLIGHTS

- A three-dimensional porous material (MWCNTs-rGO-IL) was synthesized by self-assembly.
- A new PANI-MWCNTs-rGO-IL composite coating was prepared by electrochemical method.
- It presented high thermal stability and extraction selectivity for alcohols.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, ionic liquid (IL, i.e. 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate), carboxyl multiwall carbon nanotubes (MWCNTs) and reduced graphene oxide (rGO) were used to prepare three-dimensional porous material (MWCNTs-rGO-IL) by one-step self-assembly, then it was co-electrodeposited with polyaniline (PANI) on stainless steel wires by cyclic voltammetry. The resulting coating (PANI-MWCNTs-rGO-IL) was characterized by using FT-IR and scanning electron microscopy etc, and it showed porous structure and had high thermal stability. Furthermore, it was found to be very suitable for the headspace solid-phase microextraction of alcohols (i.e. octanol, nonanol, geraniol, decanol, undecanol and dodecanol). By coupling with gas chromatography, wide linear ranges and low limits of detection (i.e. 2.2–28.3 ng L^{-1}) were obtained for the alcohols. The coating also presented good repeatability and reproducibility; the relative standard deviations for intra-fiber and fiber-to-fiber were less than 5.6% (n = 5) and 7.0% (n = 5) respectively. In addition, the proposed method was successfully applied to the determination of alcohols in tea drinks, and the recoveries for standards added were 85.6–114%.

1. Introduction

In the early 1990s, Pawliszyn et al. proposed an efficient sample-preparation method—solid-phase microextraction (SPME) and later they improved it [1,2]. Compared with other methods, such as

* Corresponding author.
E-mail address: bzzeng@whu.edu.cn (B. Zeng).

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liquid-liquid extraction [3,4] and solid-phase extraction [5–9], SPME shows some merits. It is organic solvent-free and easily coupled with chromatography etc [10]. The method has been widely applied in many fields such as biochemistry [11], pharmacy [12], food [13] and environment [14,15]. SPME is based on the distribution equilibrium of analytes between coating (or fiber) and solution (or the headspace phase above the solution) [16]. Hence, the sensitivity and selectivity of SPME mainly depend on the coating, and the exploitation of new coatings is important. Electrochemical method is useful in fabricating coatings, and a number of conductive polymers based coatings have been prepared by this means, such as polypyrrole, polyaniline and polythiophene coatings [17–20]. To improve their properties, ionic liquids (ILs), polymeric ionic liquids (PILs) [21], carbon nanomaterials [22], and metal-organic frameworks (MOFs), etc [23], were combined with them.

ILs are a special class of molten salts which consist of bigger organic cations and smaller inorganic or organic anions. They have many unique physical and chemical properties, such as low melting points, high thermal stability, nonvolatility and strong dissolution effect, thus they are considered promising extractant [24]. In recent years, they were attempted in constructing SPME coatings and showed good performance [25–27]. Furthermore, by changing the structure of ionic moieties or polymerizing, the properties of ILs can be changed to a great extent. Therefore, various ILs based coatings can be prepared and they can suit for different target analytes. Hsieh et al. developed Nafion membrane-supported IL fibers for the determination of polycyclic aromatic hydrocarbons (PAHs) in aqueous samples [28], and the extraction efficiency of three ILs was compared. Amini et al. prepared IL based SPME fibers and detected methyl *tert*-butyl ether (MTBE) in gasoline sample [29], and they concluded that the IL with longer carbon chain had higher extraction efficiency for MTBE.

Carbon nanotubes (CNTs) have out-standing mechanical, electrical and physical properties, and have attracted tremendous attention in electronics, catalysis, biomedicine and analytical chemistry [30]. CNTs possess large surface area, unique tubular structure, remarkable chemical and thermal stability and rich stacking π electrons [31], which are favorable to enrichment and separation [32–34]. By modifying the polarity, hydrophilicity and ion-exchange capability of CNTs can be altered, suiting for the SPME of different substances [35].

Graphene also has unique structure and property, such as high conductivity and thermal stability, large surface-to-weight ratio (2630 $m^2 g^{-1}$) and high affinity for organic compounds [36]. These make it a good adsorbent for SPME. Wang et al. employed a homemade graphene-coated fiber to extract 16 PAHs from cigarette smoke and it showed good performance [37]. Li et al. used aminographene to prepare SPME coating for the determination of five synthetic musks in aqueous samples by coupling with GC/MS; low limits of detection (0.46–5.96 ng L^{-1}) and wide linear ranges (5–500 ng L^{-1}) were obtained [38].

Furthermore, to improve the properties of IL, CNTs and graphene based fibers they are combined in constructing SPME fibers. As noted in literature, several IL-carbon material composites based SPME fibers were reported [39–42]. In addition, a class of novel ILs were synthesized by on-fiber preparation strategy and modified on graphene oxide (GO)-coated stainless steel wires, which were used as SPME fibers for the enrichment of polycyclic aromatic hydrocarbons and phthalate esters [43]. An on-fiber anion exchange process was utilized to alter the extraction performance of multiwalled carbon nanotubes-poly(1-vinyl-3-octylimidazolium bromide) coating [44].

In this work, a three-dimensional (3D) porous carboxyl multiwall carbon nanotube-reduced graphene oxide-ionic liquid (MWCNTs-rGO-IL) composite was prepared. Then it was co-electrodeposited with polyaniline (PANI) on stainless steel wire to prepare SPME fiber. The fiber presented high thermal, chemical and mechanical stability, long lifetime and high extraction capacity. When it was used for the determination of several alcohols by coupling with gas chromatography (GC), it showed lower limits of detection (LODs), wider linear ranges and satisfactory sensitivity in comparison with other fibers reported [27,44–46].

2. Experimental

2.1. Apparatus

A CHI 617A electrochemical workstation (CH Instrument Corp., Shanghai, China) was employed for preparing SPME fibers, and a conventional three-electrode system was adopted, including a stainless steel wire (2 cm × 250 μm O.D.) as working electrode, a Pt wire (2.5 cm × 0.1 cm O.D.) as counter electrode and a saturated calomel electrode (SCE) as reference electrode. A SP-6890 GC equipped with a flame ionization detector (FID) (Shandong Lunan Ruihong Chemical Instrument, Tengzhou, China) and N2000 chromatographic workstation (Zhenjiang University, Zhejiang, China) was used for GC experiments. The separation of alcohols was carried out on an AE.SE-54 capillary column (5% phenyl–95% methyl polysilicone, 30 m × 0.32 mm × 0.33 μm, Lanzhou Atech Technologies, Lanzhou, China). The temperature was programmed as follows: initial temperature was set at 50 °C and kept for 3 min; then the temperature was increased to 115 °C at 10 °C min^{-1}, at 5 °C min^{-1} to 200 °C, and kept at this temperature for 2 min. The total run time was about 30 min. The injector mode was splitless, the temperatures of injector and detector were 250 °C. Ultrapure nitrogen was used as the carrier at 1 mL min^{-1} and makeup gas at 30 mL min^{-1}, respectively. The SPME device was homemade, and it was a modified 5 μL syringe. The commercial SPME fiber holder (Supelco, Bellefonte, USA) and the 100 μm commercial polydimethylsiloxane (PDMS) fiber were chosen for comparison. The scanning electron microscopy (SEM) images were obtained using a Quanta-200 SEM instrument (FEI, The Netherlands). The FT-IR spectra were recorded with a Nexus-670 Fourier transform infrared spectrometer (Nicolet, USA).

2.2. Reagents and materials

Aniline (ANI) came from Sinopharm Chemical Reagent Co. (Shanghai, China). Prior to use, it was purified through vacuum distillation. Other chemicals used were of analytical reagent grade. 1-Hydroxyethyl-3-methylimidazolium tetrafluoroborate ([HOEMIm]BF_4), 1-hydroxyethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([HOEMIm]NTf_2) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF_4) were purchased from Lanzhou institute of Chemical Physics (Gansu, China). Ammonia (28 wt%) and hydrazine (35 wt%) were supplied by the Reagent Factory of Shanghai (China). GO powder (99.95%, particle size ≤30 μm) and MWCNTs (i.e. carboxyl multiwall carbon nanotubes, purity >95%, OD < 8 nm, length: 0.5–2 μm, –COOH content: 3.86 wt%) were purchased from XF NANO, INC (Nanjing, China). Octanol, nonanol, geraniol, undecanol and dodecanol were purchased from the Aladdin Chemistry Co. (Shanghai, China). Decanol was obtained from the Reagent Factory of Shanghai (China). The stock solutions (1 mg mL^{-1} for all alcohols) were prepared with methanol and they were diluted (0.01–500 mg L^{-1}) with methanol step-by-step for further use. These solutions were stored in a refrigerator (4 °C). The samples (i.e. green tea drink and black tea drink) were purchased from the local supermarket (Wuhan, China).