Graphene coating bonded onto stainless steel wire as a solid-phase microextraction fiber

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ABSTRACT

A graphene coating bonded onto stainless steel wire was fabricated and investigated as a solid-phase microextraction fiber. The coating was characterized by scanning electron microscopy and energy-dispersive X-ray spectrometer. The coating with rough and crinkled structure was about 1 μm. These characteristics were helpful for promoting extraction. Using five *n*-alkanes (*n*-undecane, *n*-dodecane, *n*-tridecane, *n*-tetradecane and *n*-hexadecane) as analytes, the fiber was evaluated in direct-immersion mode by coupling with gas chromatography (GC). Through optimizing extraction and desorption conditions, a sensitive SPME-GC analytical method was established. SPME-GC method provided wide linearity range (0.2–150 μg L^{-1}) and low limits of determination (0.05–0.5 μg L^{-1}). It was applied to analyze rain water and a soil sample, and analytes were quantified in the range of 0.85–1.96 μg L^{-1} and 0.09–3.34 μg g^{-1}, respectively. The recoveries of samples spiked at 10 μg L^{-1} were in the range of 90.1–120% and 80.6–94.2%, respectively. The fiber also exhibited high thermal and chemical stability, due to the covalent bonds between graphene coating and wire, and the natural resistance of graphene for thermal, acid and basic conditions.

1. Introduction

Solid-phase microextraction (SPME) is an innovative, solvent-free extraction technique that represents a convenient alternative to conventional extraction methods [1]. It combines sampling, concentration, matrix removal and sample introduction into one step [2,3], and easily couples to gas chromatography (GC) and high-performance liquid chromatography (HPLC). SPME involves the use of a fiber coated with a coating, which extracts different kinds of analytes from different kinds of media. The coating material determines the sensitivity and selectivity of SPME. Many coating materials have been commercialized, such as polyacrylate (PA), polydimethylsiloxane (PDMS), carboxen/polydimethylsiloxane (CAR/PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), carbowax/divinylbenzene (CW/DVB), divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and carbowax/templated resin (CW/TPR). At the same time, many novel coating materials were also researched for SPME, such as organic polymers (e. g. polypyrrole [4], polyaniline [5] and polymeric ionic liquids [6]), metal or metal oxide nanomaterials (e. g. gold nanoparticles [7], nano-structured lead dioxide [8] and TiO$_2$ nanotubes [9]), metal-organic frameworks (MOFs) [10]. Carbon-based materials

are known for their high adsorption capacity for organic compounds, and some of them, such as carbon nanotubes [11–15], nanoporous carbon [16,17], activated carbon [18], bamboo charcoal [19] and glassy carbon [20] have already been applied in SPME.

Graphene, an atomically thin honeycomb lattice of carbon atoms, has recently sparked great excitement in the scientific community discovered shortly by Geim et al. in 2004 [21]. Its essentially two-dimensional form of carbon displays excellent mechanical [22], electrical [23] and optical properties [24], which make it the most promising carbon-based nanomaterial after fullerene and carbon nanotubes. Graphene also exhibits a high surface area (2630 m^2 g^{-1}) and rich stacking π electrons [25]. Based on these superior characteristics, graphene has been applied in SPME [26,27,29–33]. Graphene was firstly coated on stainless steel wire as SPME coating by physical adsorption method [26]. Then a layer-by-layer fabrication strategy was developed to covalently bond graphene coating to the fused-silica substrate. The bond between graphene and the silica fiber improved its chemical stability [27]. However, the silica fiber is fragile and must be handled with great care [28]. Furthermore, sol-gel technique and simple and fast hydrothermal strategy were used to develop novel graphene coated stainless steel wire fibers [29–31], substrateless graphene fiber [32] and monolithic graphene fiber [33]. These fibers with graphene coating exhibited low detection limits for pyrethroid pesticides (3.69–69.4 ng L^{-1}) and PAHs (1.52–2.72 ng L^{-1}), higher extraction efficiency for organochlorine

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pesticides (OCPs) than commercial fibers (PDMS, 85 μm; PDMS/DVB, 65 μm), due to π-π stacking interaction and hydrophobic effect. Although the graphene coating provided excellent extraction efficiency, the absence of chemical bonds between the coating and stainless steel wire inevitably affects the lifetime and chemical stability.

An ideal fiber should possess high extraction efficiency, high strength and strong adhesion between the coating and substrate. Based on these considerations, this work was aimed at preparing a graphene coating bonded onto stainless steel wire as a SPME fiber. Stainless steel wire was coated with silver layer by electroless plating technique, and then a 3-mercaptopropyltrimethoxysilane monolayer was self-assembled to silver. After hydrolyzing, the silanol groups were derived from monolayer. Graphene oxide was bonded onto silanol functionalized wire through a layer-by-layer fabrication strategy, and the thickness was also easily controlled. Graphene oxide coating was converted to graphene coating by deoxidization in hydrazine. Coupled to GC, the graphene SPME fiber was evaluated using *n*-alkanes as model analytes, and the SPME-GC method was used to analyze real samples.

2. Experimental

2.1. Materials and reagents

The stainless steel wire (Φ 180 μm) was purchased from the Yixing Shenglong Metal wire Net. Co. (Jiangsu, China). *n*-Undecane (*n*-C_{11}), *n*-dodecane (*n*-C_{12}), *n*-tridecane (*n*-C_{13}), *n*-tetradecane (*n*-C_{14}) and *n*-hexadecane (*n*-C_{16}) were of analytical grade quality and purchased from Shanghai Jingchun Industry Co. (Shanghai, China). $AgNO_3$, glucose, titanium butoxide and KCl were of analytical grade quality and obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). 3-Mercaptopropyltrimethoxysilane (98%) and 3-aminopropyltrimethoxysilane (98%) were obtained from Qufu Chenguang Fine Chemical Co. (Qufu, China) and purified by vacuum distillation before use. Toluene was dried by refluxing with sodium for 24 h, and then distilled before use. Graphene oxide was prepared according to the modified Hummers method [34]. All the other chemicals were of analytical grade quality. Rain water and a soil sample from petrol station were collected locally as real samples.

2.2. Apparatus

Analysis of the model compounds was performed with an Agilent 7890 A GC system (Agilent Technologies, USA) equipped with a flame ionization detector (FID), a split/splitless inlet and a HP-5 capillary GC column (30 m × 0.32 mm i.d. × 0.25 μm film thickness). Ultrapure nitrogen (> 99.999%) was used as the carrier and make-up gas at 3 mL min^{-1} and 25 mL min^{-1}, respectively. The inlet was used in splitless mode at 280 °C. The detector temperature was fixed at 300 °C. For the chromatographic separation, the column temperature was programmed as follows: initial temperature was held at 60 °C and programmed at 10 °C min^{-1} to 160 °C, then programmed at 20 °C min^{-1} to 280 °C.

Surface properties of the SPME fiber were characterized by a field-emission scanning electron microscope (FESEM, SUPRATM55, Carl Zeiss, AG, Germany) and an energy-dispersive X-ray spectrometer (EDS, Oxford INCA X-Act, England).

2.3. Preparation of the graphene coating bonded fiber

As shown in Fig. 1, the graphene coating bonded fiber was prepared through electroless plating, layer-by-layer fabrication and chemical reduction processes successively. Electroless plating technique was applied to activate the stainless steel wire with silver [35]. Then the silanols were derived by self-assembling 3-mercaptopropyltrimethoxysilane on silver and hydrolysis [15]. Layer-by-layer strategy was applied to fabricate graphene oxide coating by immersing the silanol functionalized wire in sol-gel solution and graphene oxide dispersion in turn. The details were as follows: one end of stainless steel wire was immersed into a reaction solution containing 0.10 mol L^{-1} [Ag(NH$_3$)$_2$]$^+$ and 0.50 mol L^{-1} glucose for 3 h at room temperature; After being washed and dried, the silver coated wire was immersed into a toluene solution of 3-mercaptopropyltrimethoxysilane (20 mmol L^{-1}) for 24 h; The wire with 3-mercaptopropyltrimethoxysilane monolayer was treated using a 0.1 mol L^{-1} HCl for 2 h to obtain silanol functionalized wire; It was immersed into a sol-gel solution of titanium butoxide and 3-aminopropyltrimethoxysilane (2:3, v/v) for 10 min, and then it was dried in atmosphere for 30 min, and immersed into graphene oxide in ethanol (25 mg mL^{-1}) for 10 s. After that, the processed wire was heated under nitrogen at 100 °C for 30 min. This step was repeated five times to obtain satisfactory thickness. A black graphene oxide coating bonded onto the wire was obtained. SiO_2-TiO_2 layer formed chemical bonds with Si-OH of the wire and –COOH of graphene oxide after heating. The chemical bonding between graphene and wire improved its chemical stability. And the thickness of coating could be regulated by layer number of graphene oxide. The graphene oxide coating was reduced to graphene coating by hydrazine hydrate (50%, v/v) for 12 h at room temperature, which further increased the hydrophobicity of coating.
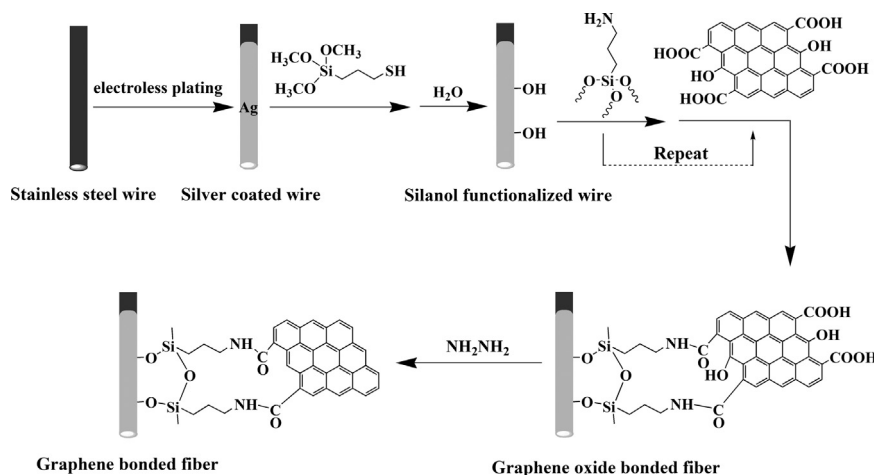

Fig. 1. Preparation process of the graphene coating bonded stainless steel wire SPME fiber.