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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.

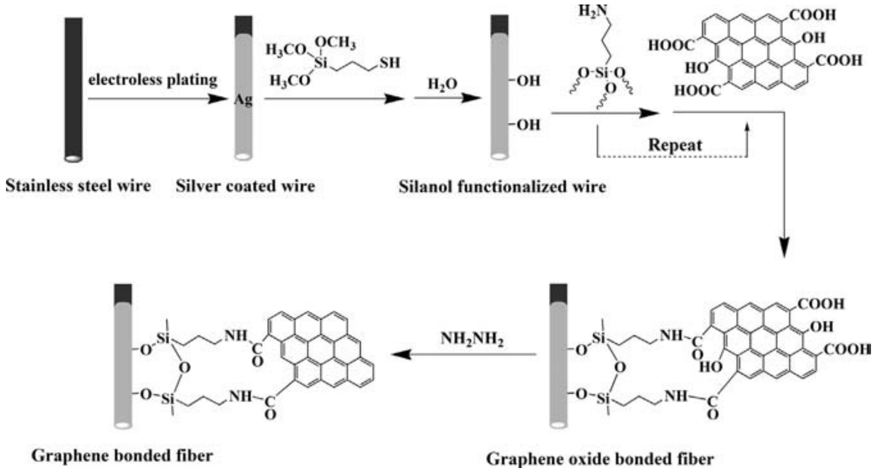

Fig. 1. Preparation process of the graphene coating bonded stainless steel wire SPME fiber.

2.4. Preparation of sample solutions

Stock solution of *n*-alkanes was prepared in ethanol at a concentration of 10 mg L^{-1} and stored at 4 °C for use. Working solutions were prepared daily by diluting the stock solution with distilled water to 10 μg L^{-1}. The dried soil (100.0 g) was extracted by soxhlet extraction method with 45 mL ethanol for 6 h. Then the extract was diluted to 50.0 mL. Subsequently, 1.00 mL of ethanol extract was diluted to 100.0 mL with water. Rain water and water solution of ethanol extract from a soil sample were used as real samples. KCl was added into working solutions and real samples to regulate ionic strength.

2.5. Solid-phase microextraction

The fiber was equipped into a homemade SPME device, which was a modification of a 5 μL syringe. Before the extraction, the fiber was aged in the GC inlet at 280 °C for 20 min. All the extractions were performed in direct-immersion mode with 10 mL aqueous solution in a 15 mL vial. A magnetic bar at 700 rpm rate was inside the vial to accelerate the extraction. After the extraction, the fiber was withdrawn into the needle and transferred into GC inlet. Then the fiber was stretched out the needle and the extracted analytes were thermally desorbed at 280 °C for 5 min. Possible carryover effect was minimized by keeping the fiber in the inlet for an additional time. The times of repetition of each data point were three.

3. Results and discussion

3.1. Characterization of the graphene coating bonded fiber

Surface structure of the SPME fiber was investigated by FESEM. As shown in Fig. 2a and b, the coating is rough and crinkled. The crinkled structure ascribed from graphene sheet edge, which increased surface area to strengthen extraction efficiency. As shown in Fig. 2c, graphene sheets were seen from the cross section of coating. Thickness of the graphene coating is about 1 μm. The thin coating is advantageous to mass transfer in extraction process. And the silver layer is about 0.5 μm.

The singles of Si, O, Ti and C were obvious in EDS spectrum of the coating (see supporting information). Singles of Si, O and Ti ascribed from SiO_2-TiO_2 layer, and C peak ascribed from graphene.

3.2. Optimization of SPME conditions

The extraction efficiency of SPME fiber is significantly influenced by several factors, such as extraction time, extraction temperature, ionic strength, stirring rate and desorption time. To achieve the best extraction efficiency, these factors were investigated and optimized.

3.2.1. Extraction time

SPME is an equilibrium-based technique, and there is fairly an optimum between the extraction amount and the extraction time. Selection of the optimum extraction time is one of the critical steps in SPME method development. The effect of extraction time

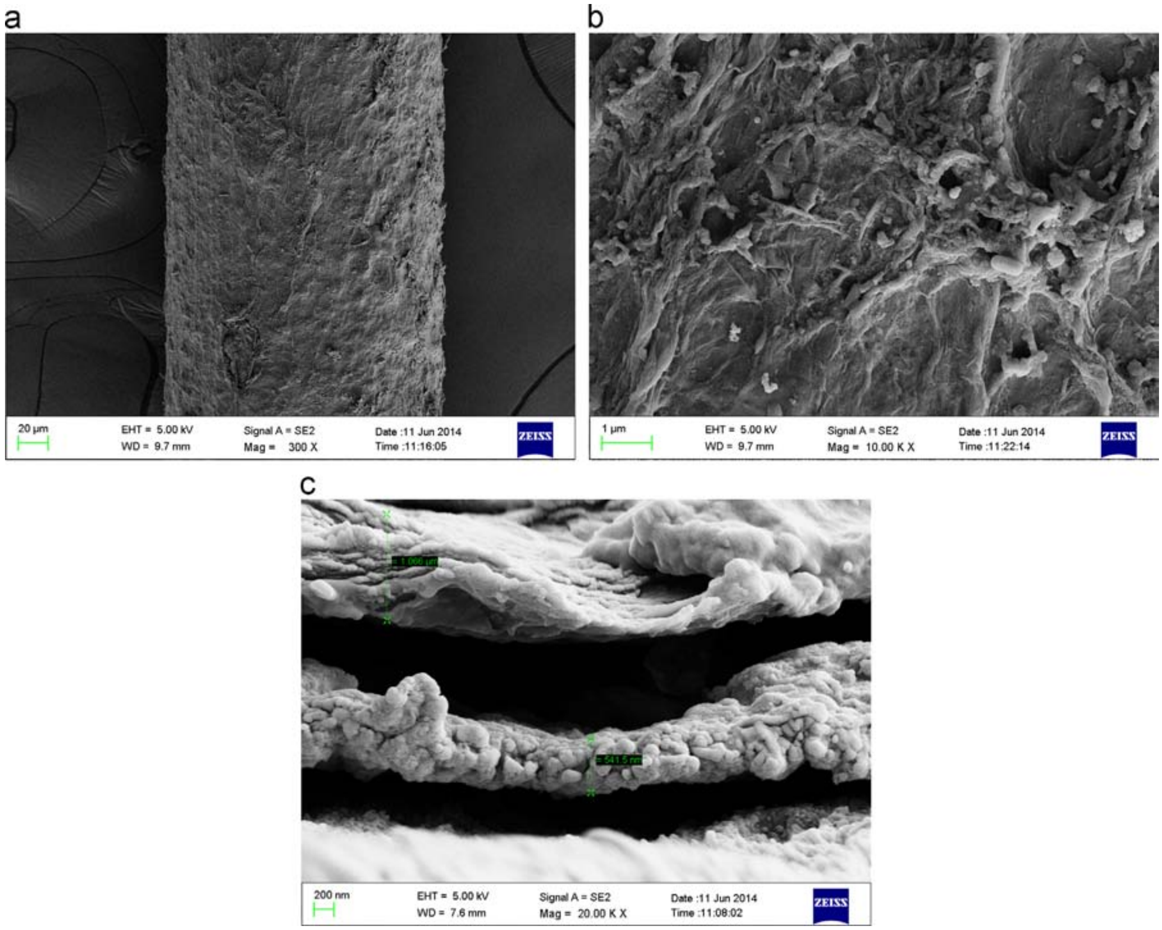

Fig. 2. SEM images of the graphene coating bonded SPME fiber with magnification at 300 (a), 10,000 (b) and 20,000 (c).

on extraction efficiency was investigated at 10, 20, 30, 40 and 50 min. As shown in Fig. 3, the highest extraction efficiency is obtained at 40 min for all analytes. 40 min was ultimately chosen as the preferred extraction time for following studies.

3.2.2. *Extraction temperature*

Extraction temperature has a twofold impact on the extraction efficiency. In general, increasing the extraction temperature can enhance the mass transfer, but partition coefficients of analytes between fiber and sample decrease. Extraction temperature profiles for five *n*-alkanes are shown in Fig. 4. Extraction efficiency of five *n*-alkanes was tested in the range of 30 to 60 °C. As shown in Fig. 4, the extraction efficiency is increased from 30 to 40 °C, and decreased from 40 to 60 °C. Then, the extraction temperature of 40 °C was chosen for the following experiments.

3.2.3. *Ionic strength*

Adding salt into the aqueous sample would reduce the solubility of organic analytes in aqueous phase due to the formation of hydration spheres around the ionic salt molecules [36], which increases their concentrations in fiber coating. The effect of ionic strength on extraction efficiency was investigated by adding different amount of KCl (0–30%, w/v) in working solution. And 30% (w/v, g mL^{-1}) KCl of solution is near to saturated solution. As shown in Fig. 5, extraction efficiencies of three analytes are increased with increasing KCl from 0 to 20% and are decreased from 20% to 30% of KCl. So, content of KCl in working solution and samples was fixed at 20% (w/v, g mL^{-1}) in all extraction processes.

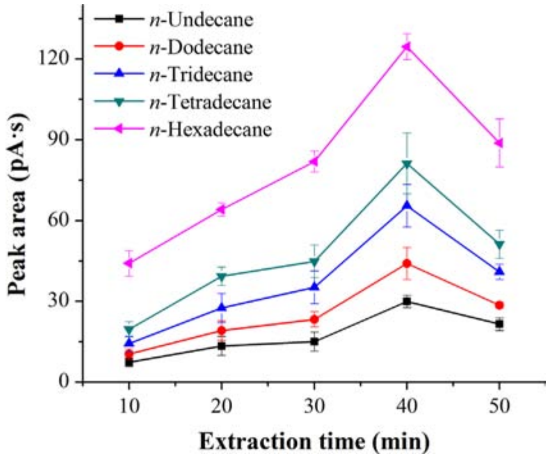

Fig. 3. The effect of extraction time on extraction efficiency. Conditions: extraction temperature, 40 °C; content of KCl, 20% (w/v); stirring rate, 700 rpm; desorption, 280 °C for 5 min; analytes concentration, 10 μg L^{-1}.

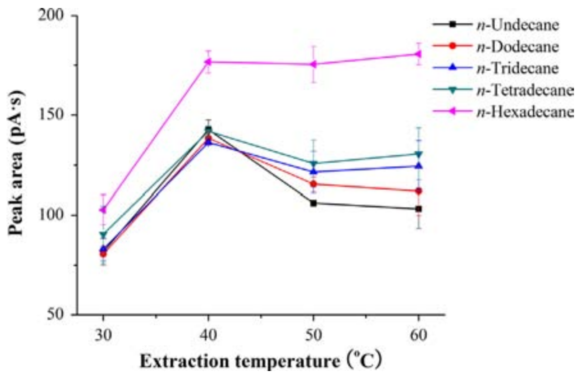

Fig. 4. The effect of extraction temperature on extraction efficiency. Conditions: extraction time, 40 min; other conditions are the same as in Fig. 3.

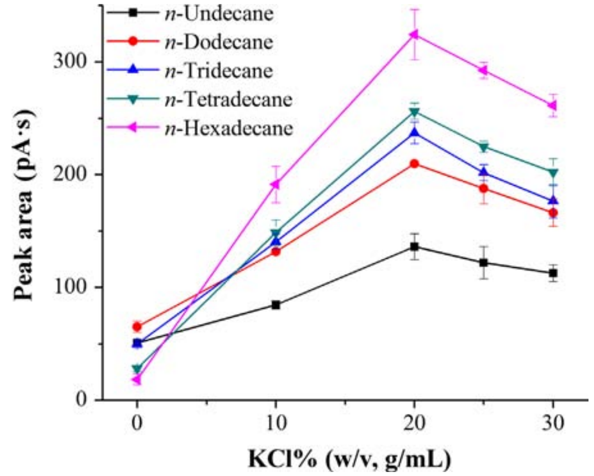

Fig. 5. The effect of ionic strength on extraction efficiency. Conditions: extraction time, 40 min; other conditions are the same as in Fig. 3.

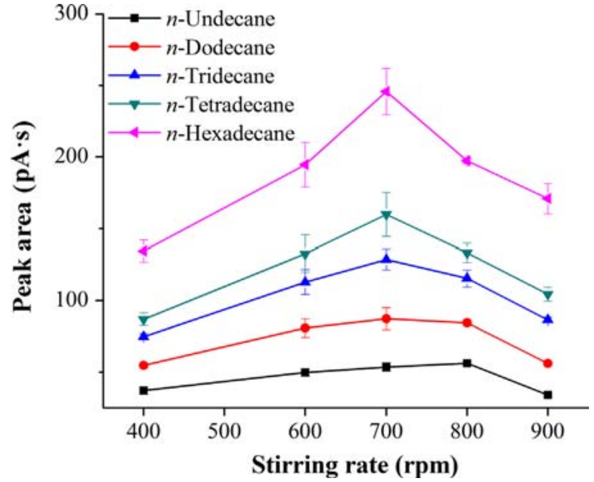

Fig. 6. The effect of stirring rate on extraction efficiency. Conditions: extraction time, 40 min; other conditions are the same as in Fig. 3.

3.2.4. *Stirring rate*

Generally, increasing stir rate can effectively accelerate mass transfer of the analyte to the extraction coating and thus enhance the extraction efficiency. The effect of stirring rate ranging from 400 to 900 rpm on the extraction efficiency was also investigated. As shown in Fig. 6, the best extraction efficiency was obtained at 700 rpm for most of analytes. When stirring rate was higher than 900 rpm, a large amount of air bubbles were observed in aqueous sample and that was unfavorable for extraction. Therefore, the stirring rate in extraction process was fixed at 700 rpm.

3.2.5. *Desorption time*

Desorption time could affect the responses of the target analytes significantly, so optimization of desorption time is very important for SPME applications. Under certain desorption temperature at 280 °C, the desorption profiles ranging from 1 to 5 min were investigated. As shown in Fig. 7, the peak area reaches a maximum at 2 min and afterward it reaches saturation. The rapid desorption of analytes was mainly attributed to the thin coating. Considering the carry-over effect, all desorption processes were performed at 280 °C for 5 min.

3.3. Method evaluation and analysis of real samples

3.3.1. Method evaluation

Under the optimized conditions, the SPME-GC analytical method was investigated by extracting a series of standard water samples ranging from 0.01 to 150 μg L^{-1}. All the results including linear range, correlation coefficient of calibration (r), limits of detection (LODs), single fiber and fiber-to-fiber repeatability are listed in Table 1. The linearity ranged from 1.5 to 150 μg L^{-1} for *n*-undecane and *n*-dodecane, from 0.8 to 150 μg L^{-1} for *n*-tridecane and from 0.2 to 150 μg L^{-1} for *n*-tetradecane and *n*-hexadecane, with all the correlation coefficients being larger than 0.9968. LODs were defined as the concentration of the analytes at three times the signal to noise ratio ($S/N=3$), which were investigated by extraction of water samples spiked at different levels to meet such signal. LODs were in the range 0.05–0.5 μg L^{-1}. The precision of the method was tested by performing nine consecutive extractions, and the RSD ($n=9$) was at the range of 8.5 to 9.6%. The RSD ($n=3$) for fiber to fiber variation was less than 12% using three different fibers prepared in the same way, which suggests that the fabrication of fiber is reproducible. The performance of the analytical method was compared with other reports [37,38] with the same analytes. As shown in Table 1, LODs of the method are much lower than that of HS-SPME-GC-FID method based on cellulose acetate-PVC coated silver fiber, and are comparable to that of HS-SPME-GC–MS method by a commercial PDMS fiber.

3.3.2. Application to real samples

To evaluate the applicability of the fiber for analyzing real samples, the SPME-GC method was applied to determine *n*-alkanes in a rain water and water solution of ethanol extract from a soil sample. The results are shown in Table 2. Five *n*-alkanes were detected in rain water ranging from 0.85 to 1.96 μg L^{-1}. These analytes were also quantified in the range of 0.09–3.34 μg g^{-1} in soil sample. Recoveries of five *n*-alkanes spiked at 10 μg L^{-1} in two water samples ranged from 90.1 to 120% and 80.6 to 94.2%, respectively. In order to validate method, a commercial PDMS fiber was used to analyze samples under the same conditions. The analysis results obtained from graphene coated fiber were comparable with that from PDMS fiber. According to the analysis results of two real samples, it is obvious that the SPME-GC method is an effective analytical method.

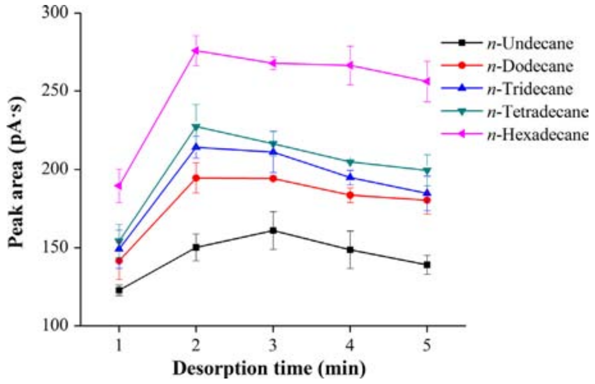

Fig. 7. The effect of desorption time on extraction efficiency. Conditions: extraction time, 40 min; other conditions are the same as in Fig. 3.

3.4. Stability of the graphene coating bonded fiber

Stability is crucial for practical application of the SPME fiber. Damage of the coating was mainly caused by its exposure to high temperature, acidic or basic solution and strong mechanical stirring during extraction processes. In order to evaluate the stability, a fiber was heated at 280 °C for 3 h, immersed in 1 mol L^{-1} HCl for 24 h and in 1 mol L^{-1} NaOH for 25 h in turn. As shown in Fig. 8, the extraction capacity of the treated fiber is not lost obviously, which demonstrated the excellent thermal resistance and chemical stability of the fiber. The high stability of the proposed fiber resulted from the chemical bond between graphene coating and wire, and the excellent resistance of graphene for thermal, acid and basic conditions.

4. Conclusions

In order to improve the lifetime and chemical stability of graphene coated fibers, a new fiber with a bonding graphene coating was developed. Electroless plating, molecular self-assembly and layer-by-layer strategy were introduced in preparation process. According to characterization by a scanning electron microscope and an energy-dispersive X-ray spectrometer, a rough and crinkled graphene coating was observed, and its thickness was about 1 μm. Coupled with GC, the fiber was investigated using five *n*-alkanes (*n*-undecane, *n*-dodecane, *n*-tridecane, *n*-tetradecane and *n*-hexadecane). The SPME-GC method presented wide linearity range (0.2–150 μg L^{-1}) and high sensitivity (LODs, 0.05–0.5 μg L^{-1}). It was applicable to analyze rain water and a soil sample. Five analytes were quantified and recoveries were also in acceptable ranges. These indicated the fiber was efficient for SPME analysis of some *n*-alkanes. The fiber exhibited high thermal and chemical stability. On the one hand excellent stability was due to the natural resistance of graphene for thermal, acid and basic conditions, on the other hand the chemical bonds between coating and wire such as Si-O-Si and CO-NH were helpful for the fiber stability. Silanol is resistant to thermal and acid conditions. And the use of TiO_2 in coating improves silanol resistance for basic conditions.

Table 1
Analytical performances of the graphene coating bonded SPME fiber and some other fibers for *n*-alkanes.

Analytes	Linear range (μg L^{-1})	LODs (μg L^{-1})	[a]Correlation coefficient (r)	[b]Repeatability (RSD %)		Cellulose acetate-PVC fiber [37]		PDMS fiber-GC–MS [38]	
				Single fiber ($n=9$)	Fiber to fiber ($n=3$)	Linear range (μg L^{-1})	LODs (μg L^{-1})	Linear range (μg L^{-1})	LODs (μg L^{-1})
n-Undecane	1.5–150	0.5	0.9968	9.0	5.6	300–3000	100	60–400	0.08
n-Dodecane	1.5–150	0.5	0.9994	8.8	3.8	300–3000	100	60–400	0.07
n-Tridecane	0.8–150	0.25	0.9989	8.5	12	150–3000	50	60–400	0.08
n-Tetradecane	0.2–150	0.05	0.9992	8.9	7.2	150–3000	50	60–400	0.07
n-Hexadecane	0.2–150	0.05	0.9997	9.6	10	150–3000	50	60–400	0.04

[a] Calibration level: $n=9$.
[b] Spiked level: 10 μg L^{-1}.

Table 2
Analysis results and recoveries for five *n*-alkanes in two real samples.

	Graphene coated fiber				Commercial PDMS fiber			
Analytes	Rain water (μg L^{-1})	[a]Recovery (*n*=3, RSD%)	Soil sample (μg g^{-1})	[a]Recovery (*n*=3, RSD%)	Rain water (μg L^{-1})	[a]Recovery (*n*=3, RSD%)	Soil sample (μg g^{-1})	[a]Recovery (*n*=3, RSD%)
n-Undecane	1.69	114 ± 5.2	0.09	80.6 ± 5.6	1.42	106 ± 2.6	[b]ND	90.5 ± 8.2
n-Dodecane	1.87	90.1 ± 2.8	0.11	83.5 ± 7.8	2.03	112 ± 3.2	[b]ND	88.6 ± 6.9
n-Tridecane	0.85	120 ± 3.6	0.66	94.2 ± 9.3	[b]ND	109 ± 6.3	0.82	85.3 ± 7.8
n-Tetradecane	0.89	111 ± 5.0	1.27	86.3 ± 7.9	[b]ND	120 ± 4.7	1.46	96.1 ± 9.0
n-Hexadecane	1.96	105 ± 6.3	3.34	88.1 ± 8.5	1.85	93.6 ± 5.8	3.68	87.1 ± 9.6

[a] Standard addition level: 10 μg L^{-1}.
[b] ND: not detected.

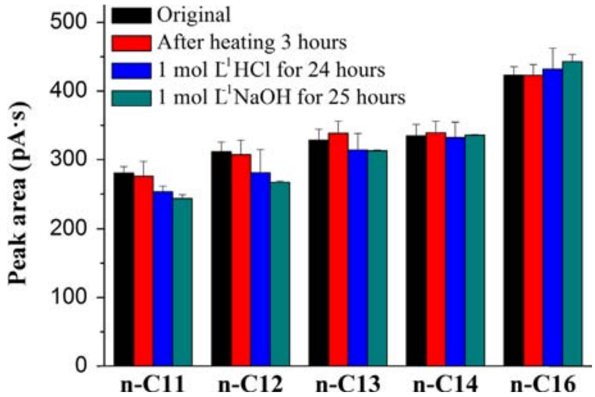

Fig. 8. The stability of the proposed SPME fiber. Conditions: extraction time, 40 min; other conditions are the same as in Fig. 3.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.11.005.

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