Talanta 119 (2014) 517–523

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Ultrafast coating procedure for graphene on solid-phase microextraction fibers

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ARTICLE INFO

Article history:
Received 25 September 2013
Received in revised form
14 November 2013
Accepted 16 November 2013
Available online 22 November 2013

Keywords:
Graphene
SPME
Fast coating
Polycyclic aromatic hydrocarbons
GC–MS

ABSTRACT

Graphene's unsurpassed specific surface area (up to 2630 m^2/g) makes it be an ideal absorbent. To promote its use as a sorption coating in solid phase microextraction, an ultrafast method was established, able to coat a stable layer of graphene on a metal fiber in only 23 s, with adjustable coating thickness between 10 and 40 μm by using sleeve barrels. The core idea includes: (1) use of semi-polymerized dimethylsiloxane as a sticky pre-liner to glue graphene and (2) rapid conversion from pre-liner to elastic polydimethylsiloxane (PDMS) to fix the glued graphene. Ultrafast conversion of the pre-liner to PDMS was achieved by direct heating of the metallic fibers. The method produced very stable and durable fibers, capable of being used for at least 120 extractions–desorption cycles and stored at room temperature for at least 20 months. Interestingly, the new method could always coat a layer of mossy graphene on the fibers to largely increase their extraction capacity. Their limit of detection reached 2 pg/L PAHs, being about 3 orders of magnitude better than that of the reported graphene-based fibers. They were applicable to the direct extraction of trace PAHs in beverages, with a linear regression range from 10 to 1000 pg/L, and recoveries of 88.9–105.3%. The relative standard deviations of peak area were 2.9–8.9% for the same fiber and 3.0–10.0% for different fibers. The method is also suitable for re-coating a used fiber and extendable to fast coating other solid sorbents on heat-resistant supports.

1. Introduction

Graphene is a monolayer of carbon atoms arranged in a two-dimensional honeycomb crystal lattice and has sparked much research interest from its unique electronic characters and intriguing quantum effects [1–3], and from its exceptional thermal and mechanical properties [4–6]. Its ultrahigh specific surface area, up to 2630 m^2/g [7], potentially makes it be an ideal high capacity sorbent. With a large delocalized p-electron system, graphene has high affinity toward carbon-based ring structures such as polycyclic aromatic hydrocarbons (PAHs) which may appear in biological systems and environments [8–10]. PAHs were thus selected as the testing samples in this study because of their chemical affinity to graphene [11], importance as environmental toxins, carcinogens, and mutagens [12], and from the need to develop better methods to monitor their concentration in the environment [13–16].

In fact, graphene has already been tried as a new sorbent to extract organic compounds by solid-phase extraction [17,18], solid-phase microextraction (SPME) [11,19–22], or stir rod sorptive extraction [23]. It is commonly used after deposition on solid supports [11,20,21] through either chemical reactions [11] or gluing [20,21]. Chemical methods can firmly immobilize graphene on the supporting surface with coating thickness tunable through layer-by-layer reaction(s) [11], but at the cost of slow speed (hours – days). Gluing is a fast strategy. It needs less than an hour [20] but may cause coatings to crack or shed during usage. We found that such damages were worsened during heating cycles when the fibers were subjected to gas chromatography (GC) where analytes are often extracted at a low temperature and desorbed at a high temperature (up to near 300 °C). The coatings will finally peel off the supports. The wide temperature shifts because of frequent absorption–desorption cycles can induce further cracks in the coatings (via contraction and expansion), eventually causing the graphene to peel off the supports. By the way, it should be mentioned that the reported graphene-fibers have not yet shown extraction efficiency as high as expectance, living a large room for further exploration.

To overcome these problems, we have devised a way to quickly replace the cracked extraction needle by chemically coating with

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http://dx.doi.org/10.1016/j.talanta.2013.11.047

graphene on the outside layer of polydimethylsiloxane (PDMS) [24]. It worked well, but the holders had to be redesigned and fabricated in laboratory, and the coating procedure remained slow (several hours). As an alternative, we propose a different concept to "renew" the needle, which is to fast coat or re-coat the needle with graphene instead of replacing it. To achieve the goal, we combined the merits of chemical and gluing coating techniques. Our strategy is to glue the graphene on a sticky but polymerizable pre-liner. The pre-liner is then forced to convert to elastic and heat-durable liner to sustain temperature-induced contraction/expansion and to fasten the glued graphene on the elastic layer, which also prevents the coatings from cracking and peeling off.

The key is thus to find a suitable pre-liner and after some trials, semi-polymerized dimethylsiloxane (s-PDMS) was found to work properly. s-PDMS is a sticky, polymerizing matter able to strongly glue graphene, and it was expected to be capable of holding the glued graphene because it will change to elastic PDMS after completion of its polymerization. At the very beginning, we also found that by using s-PDMS, both the liner and its outer glued graphene could be shaped easily by sleeve barrels and stably fixed, but the coating was not as fast as we hoped because the polymerization from s-PDMS to PDMS took several hours. Further investigations were thus systematically conducted, and different methods were tested to speed up the polymerization. Some of the methods were adaptable in a practical sense, for example, accelerating the polymerization by oven heating or by using a hair dryer.

In this paper, we discuss an ultrafast method to coat a stable layer of graphene on SPME fibers with s-PDMS as a pre-liner. The core idea is to accelerate the polymerization by directly heating the SPME fibers. As expected, the coating time was shortened to only 23 s in total, with coating thickness adjustable between 10 and 40 μm. The resulting fibers were reusable for more than 120 cycles of extraction followed by desorption at 280 °C in the injector port of a gas chromatography–mass spectrometry (GC–MS). Interesting, the new fibers acquired a layer of mossy coating. Their extraction capacity, detection sensitivity and extraction kinetics were dramatically increased and applicable to the direct extraction of trace PAHs in some beverages.

2. Experimental sections

2.1. Chemicals and materials

A standard mixture containing 16 PAHs were purchased from Sigma-Aldrich (Bellefonte, PA, USA), which contains naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorine (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3–cd]pyrene (IPY), dibenz[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BPE) at different concentrations as shown in Table 1. PDMS monomer and curing agent were purchased from Dow Corning Corporation (Midland, MI, USA). Graphite powder (99%), cyclohexane (> 99.5%), hydrazine solution (35%), $KMnO_4$ (98%), H_2SO_4 (98%), $K_2S_2O_8$ (99%), H_2O_2 (30%), HCl (37%) and phosphorus pentoxide (P_2O_5, 99%) were obtained from Beijing Chemical Reagent Factory (Beijing, China). Ammonia solution (28%) was purchased from Alfa Aesar (Lancs, United Kingdom). All the chemicals and reagents were used as received, without further purification. Aqueous solutions were prepared with pure water (> 18.2 MΩ.cm) from a Milli-Q academic system (Billerica, MA, USA).

Stainless steel wires were from Wuxi Jiajian Medical Instrument Co., Ltd. (Jiangsu, China).

2.2. SPME–GC–MS

All separations were conducted on a QP2010 Plus GC–MS system from Shimadzu (Kyoto, Japan) fitted with a DB-5 (Ultra Inert) fused silica capillary column (30m × 0.250 mm I.D. × 0.25 μm film thickness) from Agilent J&W (CA, USA). The analytes were adsorbed onto the fiber by direct immersion SPME (DI-SPME) in 25 mL aqueous sample solution, and then thermally desorbed in the injector port at 280 °C for 2.0 min in splitless mode. The carrier gas used was helium at 1.0 mL/min flow rate. The column temperature was first maintained at 60 °C for 3 min, then raised to 280 °C at 10 °C/min and held until all peaks were eluted. The separated peaks were detected by MS in selective ion monitoring mode at a detector voltage of 0.7 kV and GC–MS interface temperature at 280 °C. An electron impact ionization source was used and operated at 70 eV and 200 °C.

2.3. Preparation of SPME fibers.

2.3.1. Synthesis of graphite oxide and graphene [25–27]

To synthesize graphite oxide (GO), graphite powder (2.00 g) was added into stirred solution of 3.00 mL H_2SO_4 (98%) containing 1.00 g $K_2S_2O_8$ and 1.00 g P_2O_5 at 80 °C. After the solution turned dark blue, it was cooled to room temperature at a rate of 8 °C/h, slowly diluted with 10 mL water, filtered, washed with water until pH 7, and finally dried by natural evaporation. The obtained powder (0.50 g) was added to 12.50 mL ice-cooled (0 °C) 98% H_2SO_4 while stirring, followed by slow addition of 1.50 g $KMnO_4$ (to keep the solution temperature below 20 °C). After stirring at 35 °C for 2 h, the reaction was slowed down by dilution with 23 mL water, and 15 min later, it was terminated by further addition of 70 mL water and 1.25 mL H_2O_2 (30%). To harvest GO, the solution was acidified with 125 mL HCl (3.3%), filtered, dialyzed against water (to remove salts and acids), rotary-evaporated, and dried by lyophilization.

To prepare graphene, the dried GO was re-dispersed in water by ultrasonication to form a 0.05 wt% solution. An aliquot of 30 mL of the solution was sequentially mixed with 30 mL water, 30 μL hydrazine (35 wt%) and 210 μL ammonia (28 wt%), and kept at 95 °C in an oil bath for 1 h. Graphene was formed and collected by filtration after the solution was cooled. Graphene powders were obtained by lyophilization (ca. 2 days).

The reactions were monitored by UV–vis spectrometry on TU-1900 UV–vis spectrophotometer from Beijing Purkinje General Instrument Co. (Beijing, China), and the obtained graphene and GO were characterized by X-ray diffraction on a Rigaku D/max-2500 (Rigaku, Japan) using Cu Kα (1.5406 Å) radiation, by Raman scattering on a Renishaw in Via plus (Renishaw, United Kingdom) with 633-nm laser, and by atomic force microscope (AFM) on Veeconanoscope IIIa form Digital instruments (New York, USA). The related characterization data in the preparation of graphene by reduction of GO are as follows: UV absorption of GO at 231 nm and graphene at 270 nm. The (002) X-ray diffraction peaks for graphite, GO and graphene, respectively at 26.52°, 10.18° and 24.13°. The characteristic Raman peaks for graphite at 1582 cm^{-1} and 1350 cm^{-1} (weak), for GO at ~1350 cm^{-1} and ~1575 cm^{-1}, and for graphene at ~1350 cm^{-1} and ~1595 cm^{-1}[28]. The formed graphene nanosheets were folded, having 2.0 nm thicknesses.

2.3.2. Preparation of s-PDMS

PDMS monomer (1000 μL) and curing agent (100 μL) were mixed thoroughly, and degassed by vacuum for 30 min. The resulting s-PDMS was ready for direct use and can also be stored at −20 °C for later use for at least 6 months. It can be forced to finish its polymerization by heating to form PDMS. On a metallic

Table 1
Analytical performance and results of graphene-coated SPME fibers coupled with GC–MS in the analysis of PAHs.

No.	Compound	C_o[a] (μg/mL)	k_i[b]	Working equation[c]	R^2	LOQ[d] (pg/L)	LOD[e] (pg/L)	RSD (%)[f]		Real samples[g]					
								Same fiber (n=3)	Varied fibers (n=5)	Ice Tea			Green Tea[j]	Coca Cola[j]	Pepsi Cola[j]
										C[h] (pg/L)	Recovery (%)[i]	RSD (%)			
1	NAP	1010	10.05	y=211.5x -1179	0.9998	15	4	5.5	3.2	nd	91.3	5.3	nd	nd	nd
2	ANY	2017	20.07	y=785.3x +16448	0.9998	15	2	4.7	3.3	416	92.5	4.0	nd	nd	nd
3	ANA	1012	10.07	y=636.3x +7042	0.9998	15	2	5.9	4.1	32.8	90.3	4.9	nd	nd	nd
4	FLU	200.6	1.996	y=190.2x +3169	0.9995	15	4	6.7	8.9	nd	89.9	5.2	nd	nd	nd
5	PHE	100.5	1	y=144.3x +587.3	0.9997	10	4	5.8	8.0	nd	95.7	6.1	27.8	16.0	792
6	ANT	101.0	1.004	y=204.2x +497.3	0.9997	10	4	4.1	7.0	nd	89.8	4.9	nd	nd	nd
7	FLT	199.8	1.978	y=485.2x +2099	0.9998	15	2	3.0	6.5	nd	97.3	4.6	nd	14.7	102
8	PYR	101.5	1.010	y=328.3x +529.4	0.9997	10	2	3.3	6.6	23.9	102.6	5.0	nd	nd	nd
9	BaA	100.6	1.011	y=734.8x +2436	0.9994	10	2	2.9	6.0	nd	93.2	8.5	39.8	nd	nd
10	CHR	103.0	1.025	y=545.0x -245.2	1	10	2	3.5	4.2	17.2	98.8	6.0	nd	nd	nd
11	BbF	193.4	1.924	y=405.6x -2131	0.9999	15	2	5.4	3.0	nd	92.6	6.9	nd	nd	nd
12	BkF	98.9	0.9841	y=510.9x +751.1	0.9985	10	2	4.0	6.0	nd	93.6	7.5	nd	nd	nd
13	BaP	105.4	1.049	y=363.6x -1367	0.9986	10	2	3.7	10.0	nd	90.8	3.8	nd	nd	nd
14	IPY	97.4	0.9692	y=210.0x +1241	0.9998	10	2	6.0	6.7	nd	105	6.2	nd	nd	nd
15	DBA	201.1	2.001	y=234.1x +1971	0.9995	15	4	8.9	6.4	nd	96.9	5.4	nd	nd	nd
16	BPE	199.7	1.987	y=567.9x -909.7	0.9991	15	4	7.4	7.2	nd	98.5	3.9	nd	nd	nd

[a] Initial concentration.
[b] $k_i=(C_o)_i/(C_o)_{PHE}$.
[c] The equation's linear range was (10–1000)k_i pg/L.
[d] Limit of detection.
[e] Limit of quantification.
[f] Measured from the standard sample within a day for a same fiber and among days for different fibers.
[g] Bought from Beijing local supermarket.
[h] Concentration.
[i] Measured by spiking c_{PHE}=1 μg/L PAH standard into Ice Tea at a volume ratio of 1:25000.
[j] All data were averaged over 3 replicates with RSD <8%.

fiber, the formed PDMS will lose its stickiness and cannot be removed by gently rubbing with fingers.

2.3.3. Coating graphene or GO on SPME fibers

To start preparation, a metal or stainless steel fiber with a radius of r_f was plugged through a sleeve barrel with an inner radius of $r_s=(r_f+d_s)\pm 1$ μm, where d_s is the thickness of liner. The fiber tip was heated to red (ca. 3 s in the flame of alcohol burner, note: the flame should be stable, not against wind), dipped in s-PDMS for 1 s, pulled out of the barrel (ca. 1 s), and immediately inserted into graphene powder at 1 cm depth. After being whirled for 10 s, the fiber head was gently rotated into and out of another sleeve barrel (ca. 3 s) with an inner radius of $r_g=(r_s+d_g)=(r_f+d_s+d_g)\pm 1$ μm (where d_g is the designed thickness of graphene coating) to remove the excessive powder off the surface. The fiber was burnt again, for about 5 s, at the uncoated part (1 cm away the coating) to forcedly complete the polymerization of the pre-liner. This protocol was also used to fast prepare graphene oxide (GO), PDMS and other powder coatings.

The resulting fibers were characterized by thermogravimetric analysis (TGA) [29] and scanning electron microscopy (SEM) [11]. TGA was performed on P1 Pyris 1 TG Analyzer from Perkinelmer (Massachusetts, USA) by heating the samples from 50 °C to 600 °C at +10 °C/min under a flow of nitrogen gas. SEM was conducted on JSM-6701F from JEOL (Tokyo, Japan) operated at 10.0 kV.

2.4. Preparation of samples

A stock solution of 16 PAH standards were initially prepared in 1:1 (v/v) methanol/methylene chloride and stored at 4 °C. To prepare working solutions, the stock solution was first diluted to about 50 ng/L with methanol and then to the final concentration with water. For convenience, the concentration of PAHs, c_i (i=1, 2… 16), was indicated by $k_i c_{PHE}$, where c_{PHE} is the concentration of PHE and k_i is the ratio of a PAH's content over c_{PHE} (Table 1, column 4).

2.5. Extraction of samples

All aqueous samples were subjected to DI-SPME [30–32] without any further treatment. An aliquot of 25 mL sample solution was subjected to DI-SPME at 45 °C under agitation at 300 rpm for 45 min. To measure recovery, a sample was spiked, before DI-SPME, with a PAH standard solution (c_{PHE}=1 μg/L) at a volume ratio of 1:25000.

3. Results and discussion

3.1. Fast coating of graphene with s-PDMS as a gluing pre-liner

It is known that PDMS is polymerized from dimethylsiloxane with a curing agent through a fairly long period of time, and during this polymerizing process, s-PMDS forms and exhibits an adhesive property until it finally changes to PDMS. We thus tried to use this s-PDMS as a pre-liner to adhere graphene. The coating procedure was easy to manipulate but not as fast as we hoped because the change of s-PDMS to PDMS is slow in common cases. Thus, our main focus was to speed up the polymerization. Several techniques were employed, of which temperature regulation was the most effective and convenient. By elevation of temperature from 25 °C to 60–80 °C (in an oven), the polymerization was shortened from overnight to only ca. 2 h. We then tried to further increase the temperature but the limiting factor was the holders used which could melt or be damaged at high temperatures.

A short duration of directly heating the fiber was thus tried based on the supposition that a thin film will finish its polymerization in much a shorter time than a thick one if the polymerizing reaction can spread out constantly once it starts. For example, if a 1-cm s-PDMS can finish its polymerization in 2 h, then a 20-μm s-PDMS will finish its polymerization in about 15 s ($20\ \mu m \times 2\ h \times 3600\ s/10^4\ \mu m = 14.4\ s$). This was achieved by direct heating of the fiber just apart from the coatings: the polymerization of a 20-μm s-PDMS thin film was reduced to ca. 20 s at 60–80 °C and ca. 10 s at 150 °C and even 5 s at the temperature of alcohol flame (Fig. 1). In this last case, a graphene-coated fiber could be fabricated in 23 s in total, much faster than that of similar adhesive methods (10–15 min coating plus ca. 12 h solidification) [19,21] or other methods (28–80 h) [11,14]. To the best of our knowledge, this is at present the fastest method to prepare a graphene-coated SPME fiber.

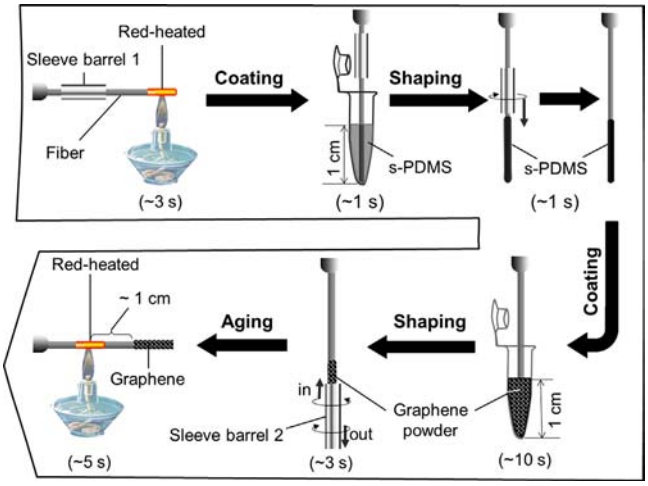

Fig. 1. Schematic steps for coating graphene on a SPME fiber.

It is worth noting that the newly formed PDMS is elastic and cannot be rubbed off by rolling on a sticky surface. This was a way to verify the completion of polymerization.

3.2. Regulation of coating thickness

Coating thickness largely impacts the extraction capacity and adsorption/desorption dynamics of SPME fibers [33,34]. Thus a coating thickness is desired to be adjustable. With the new method, the coating thickness of either PDMS or graphene (Fig. 2A) could be designed and regulated. This was achieved by simply varying the internal diameters of the sleeve barrels in between 10 and 40 μm (Table 2) and was confirmed by SEM (Fig. 2B and C). It should be noted that this regulation was reproducible, but not very accurate (ca. ± 5 μm in thickness). To have better accuracy, the sleeve barrels need to be more precisely machined, with an error $< \pm 1$ μm. Thicker coatings could still be adjusted but are limited by the size of graphene and the needle used. In fact, the thicker is a coating, the slower will the extraction kinetics become.

Table 2
Impact of coated thicknesses of PDMS liner and graphene on the extraction efficiency of benz[a]anthracene (BaA), chrysene (CHR) and benzo[a]pyrene (BaP) indicated by GC–MS' peak area.

No.	Coating thickness		Peak area ($\times 10^6$, $n=3$, RSD < 8%)		
	PDMS liner	Graphene	BaA	CHR	BaP
1	35	9	2.46	4.28	1.43
2	12.5	12.5	2.88	4.43	2.64
3	25	25	3.41	5.15	2.98
4	25	32	5.38	6.92	3.99
5	35	35	5.57	7.25	4.28
6	35	35	5.53	7.25	4.29

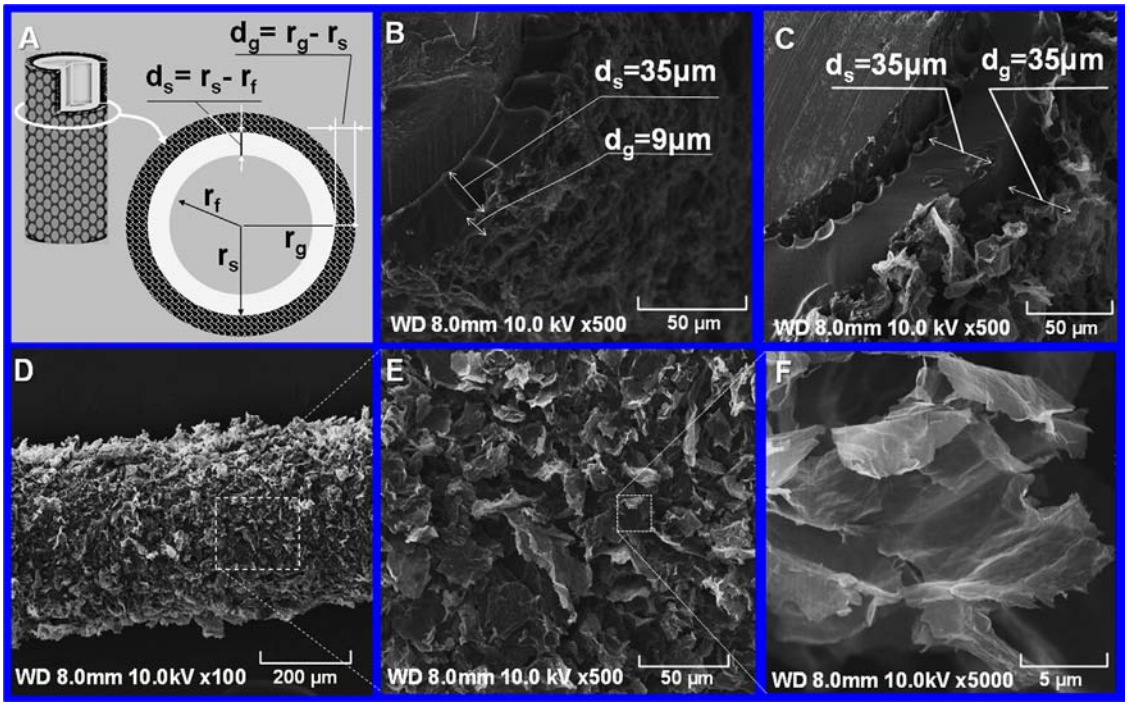

Fig. 2. Designed (A) and prepared (B–F) graphene-coated fibers with SEM images measured at the cross-sectional (B–C) and lateral (D–F) directions. Moss-like graphene surfaces, full of nanocavities, were revealed at different scales of amplification. r_f, r_s and r_g are the radii of a fiber without any coating, and with PDMS and graphene coatings, respectively; the thickness of the coating is d_s for PDMS and d_g for graphene and their illustrated data were measured according to the image obtained.

Table 2 shows that the PDMS coating has nearly no contribution to the extraction which is clarified by comparing the data in line 1 (or 3) with those in line 3 (or 5 and 6). Ideally, the extraction efficiency of graphene coating increases with its thickness, which can be validated by comparing the data in line 4 and 1 with line 5 or 6. For convenient manipulation, it is proposed to coat PDMS in 25–35 μm thickness as a liner and 35 μm graphene thickness as an extraction layer. Multilayer coatings were also obtained by the new method but not recommended because the monolayer coating of graphene is sufficient for present applications.

It should be noted that the sleeve barrels could not only regulate the coating thickness but also shave off the extra s-PDMS to form a smooth surface of PDMS (Fig. 3A). Without sleeve barrels, undesired coating shapes were obtained, often with a string of irregular droplets or bubbles (Fig. 3B).

3.3. Stability

The so-called stability of a fiber here refers to its thermal resistance, shelf life, and reusability (extraction–desorption cycles). The thermal resistance was checked by thermogravimetric analysis which showed that the obtained fibers (Fig. 4, solid line) combined the features of PDMS (Fig. 4, dot dash line) and graphene (Fig. 4, dash line), having only about 1.5% (w/w) thermal loss at 300 °C (for 10 s), which is sufficient for GC analysis. This thermal resistence is at least comparable with the chemically immobilized graphene fibers [11].

The prepared fibers could be used for at least 120 replicate extractions without obvious loss of performance (Fig. 5A–D), which is better than some commercial fibers (about 100 replicates). The fibers could also be stored at room temperature for more than 20 months and shown to be reusable after re-conditioning at 280 °C for 1 h (Fig. 5E). The extraction cycle was studied by SPME–GC–MS using real samples spiked with 200 pg/L standard phenanthrene (PHE). The relative standard deviation (RSD) of peak area of PHE was below 8.9% for run-to-run detection with a same fiber, and below 10.0% with fibers prepared in five different batches (between days). This makes the fiber adoptable for practical use and is comparable with the reported data [11]. More detailed information on RSD was shown collectively in Table 1.

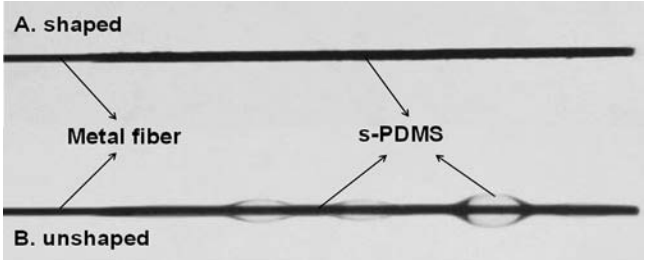

Fig. 3. s-PDMS-coated fiber shaped with (A) and without a sleeve barrel (B). The pictures were taken by Canon digital camera 450D (Nagoya, Japan).

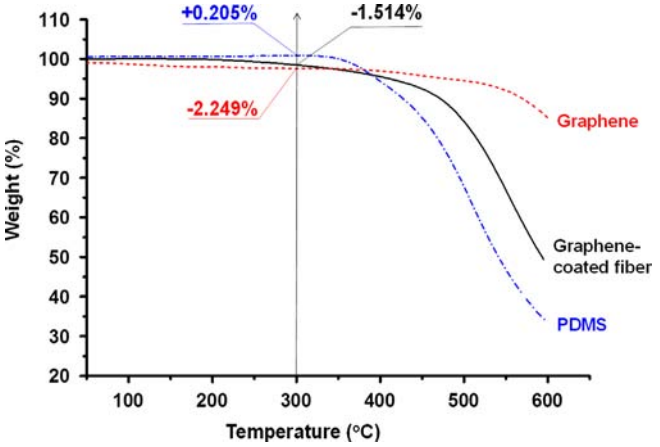

Fig. 4. Thermogravimetric curves of PDMS–graphene-coated fiber (solid line), PDMS (dot dashed line) and graphene (dashed line) measured at a heating rate of 10 °C/min in nitrogen gas atmosphere.

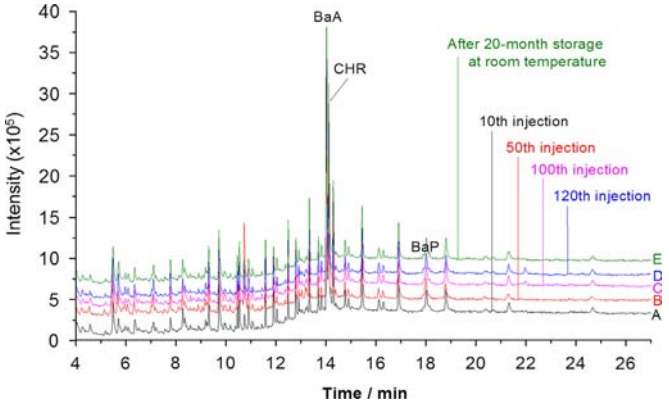

Fig. 5. Chromatograms from replicate injections with the same newly prepared SPME fiber (A–D) and stored for 2 years (E) after DI-SPME of PAH standards at $10k_i$ μg/L and 45 °C for 45 min.

There are several possible mechanisms responsible for stabilizing the coatings. Firstly, the sticky and polymerizable s-PDMS can strongly glue the graphene; secondly, the strong elasticity of the formed PDMS liner can "fasten" not only the inserted graphene molecular sheets but also causes the inner fiber body to maintain its integrity (is crack-free) against extreme temperature variation. Thirdly, the inert chemical properties of PDMS and graphene can strengthen both the liner and functional coating to resist thermal degradation; and fourthly, direct heating the metallic fiber could create a sharp radial temperature gradient across the metal fibers, inducing radial accelerated polymerization of s-PDMS, which should facilitate an inward movement of s-PDMS to compensate for the volume loss (if it exists) and result in formation of a crack-free liner (Fig. 3).

3.4. Extraction performances and comparison

By new method, the PDMS liner formed a bubble-free compact layer around the fibers (Fig. 2B or C and Fig. 3A), while the graphene sheets nearly all "plant" on PDMS, creating a moss-like surface with the graphene "leafs" almost erects or unburied (Fig. 3D and F). This moss-like graphene layer endows the fibers full of nanofoveola which are highly preferred for fast kinetics and high-capacity of extraction [33,34]. It is due to this moss-like surface that the new fibers could be used to extract both high and low concentrations of PAHs, at least up to 10 mg/L and down to ca. 2 pg/L PAHs. The enrichment factor was about 10^6–10^7 folds higher than direct injection GC–MS which offered a limit of detection (LOD) at about several μg/L PAHs and about 1000 folds higher than reported fibers which reach the LOD at a level of around 1 ng/L [11].

The impacts of extraction temperature, and the adsorption and desorption time were checked. These factors could all raise the extraction efficiency quickly at the beginning phase but soon slows down after they passed the point of 25 °C, 15 min extraction and 1.5 min desorption, respectively. These three factors turned earlier than the data in literature [11] in respect of extraction kinetics, which was ascribed to the moss-like graphene surface (Fig. 2) created on the fibers. Such a moss-like extraction surface can offer

free or loose routes for molecules to diffuse in and out rapidly. To ensure full and fast extraction of analytes, the extraction temperature was finally set at 45 °C, extraction time at 45 min and desorption time at 2 min.

In short, the fibers with moss-like graphene-coating have shown quite an ideal extraction performance, outclassing GO- and PDMS-coated fibers in extraction of PAHs, giving an order of graphene ≫ GO > PDMS (Fig. 6). Quantitatively, the graphene-based fibers produced 73.02–2507 folds higher peak areas than the PDMS-fibers or 37.23–621.4 folds higher than GO-fibers. Fig. 6 also illustrates that the liner of PDMS does not impact on the extraction of PAHs in spite that it is just beneath the moss-like graphene layer.

3.5. Analysis of real samples

To validate the real applicability of the new fibers, extraction of trace PAHs in tea productions that cannot be realized by common fibers was conducted. Fig. 7 shows the enriching and simplifying effect of SPME in the analysis of an Ice Tea sample: the chromatogram is complicated before SPME (Fig. 7A), but becomes clean and simple after DI-SPME. The results of the DI-SPME by PDMS fiber (Fig. 7B) and graphene-coated fiber (Fig. 7C) show the graphene-coated fiber combines the advantages of both graphene and PDMS. The peak

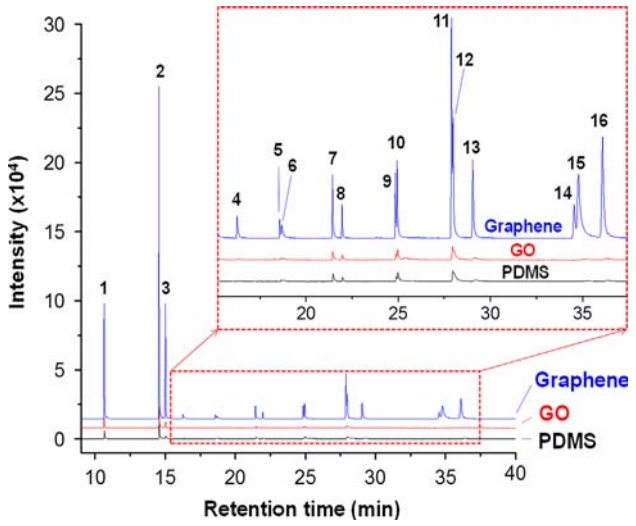

Fig.6. Chromatograms of 16 PAHs obtained after extraction by graphene-, GO-, and PDMS-coated fibers.

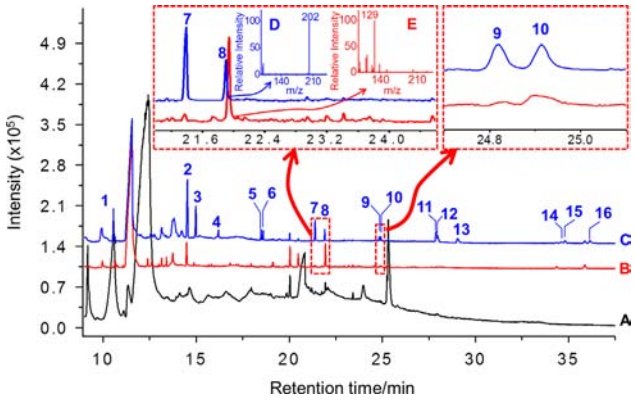

Fig. 7. Chromatograms obtained by (A) direct injection, (B) DI-SPME of an Ice Tea with a PDMS fiber, and (C and D) DI-SPME of an Ice Tea with a graphene-coated fiber. D was measured from PAHs-spiked Ice Tea. E and F show the mass spectrogram of B and C during the retention time of 21.7–22.0 min.

during the retention time of 21.7–22.0 min of DI-SPME from Ice Tea is not the target peak (Fig. 7E), which can be compared with the spiked sample (Fig. 7D). The highest contaminant in Ice Tea was ANY (at 0.42 ng/L) but still below 10 ng/L of the Standards for Drinking Water Quality of China (GB 5749-2006 [35]). To further validate its applicability, some beverage samples were assayed and the results were collectively shown in Table 1. The recoveries measured by spiking approach were 89–105%, the linear working range was in between 10 and 1000 pg/L PAHs, and R^2 was commonly higher than 0.999.

4. Conclusions

The proposed method can fabricate graphene-coating onto SPME fibers in 23 s in total, which is much faster than reported methods [11,14,19,21], being the fastest one to the best of our knowledge. The coated fibers with favorable moss-like surface enable superb functionality and have further increased the extraction performance and detection sensitivity, with LOD down to ca. 2 pg/L PAHs which is much better than the reported and/or commercial fibers [11,14,19,21]. They are hence applicable to the direct determination of trace PAHs in aqueous samples such as beverages. The SPME fibers are also very stable, able to be used for at least 120 replicate cycles of extraction/desorption at 280 °C, and to be stored for at least 20 months at room temperature, which is better than or at least comparable with the commercial fibers. The coating method is also suitable for fast coating PDMS, GO or other powder/particle materials on fibers sustainable to direct heating, which is more universal than some of the existed methods [11,14,19,21].

Acknowledgments

This work was supported by the NSFC (Nos. 21235007, 91117010, 21027003, and 21205140), MOST (No. 2012IM030400) and CAS. Miss Lijuan He and Mr. Daiqing Chen of our Institute were specially acknowledged for their donation of facilities to characterize some of the prepared fibers. Thanks to Dr. Jacob Wickham for improving the English in this paper.

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