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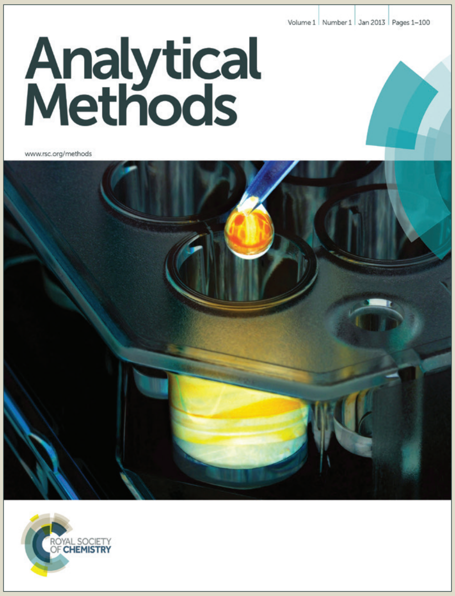

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Self-assembly of mercaptoundecanol on cedar-like Au nanoparticles coated stainless steel fiber for selective solid-phase microextraction

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Abstract: A novel organic-inorganic composite coated fiber was developed by direct chemical deposition of Au nanoparticles (AuNPs) followed by self-assembly of mercaptoundecanol using an etched stainless steel (ESS) wire as a supporting substrate for selective solid-phase microextraction (SPME). The ESS wire offered very large contact surface for subsequent growth of AuNPs in chloroauric acid solution. As a result, a uniform AuNPs coating with cedar-like structure was formed on the ESS wire and used as an alternative substrate for self-assembly of mercaptoundecanol (HS-C_{11}-OH) via Au-S bonding. The mercaptoundecanol modified AuNPs coated ESS (ESS/AuNPs-S-C_{11}-OH) fiber was then assessed for SPME of ultraviolet filters, phthalic acid esters and polycyclic aromatic hydrocarbons (PAHs) coupled to high-performance liquid chromatography with UV detection. This fiber exhibits high extraction capability and better selectivity for PAHs. Moreover main

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parameters affecting extraction were investigated and optimized. Under the optimized conditions, the developed method showed good linearity between 0.05 and 300 μg L^{-1} with corresponding coefficients in the range of 0.9973-0.9992. The limits of detection ranged from 0.010 to 0.044 μg L^{-1}. The relative standard deviation for fiber-to-fiber reproducibility of five fabricated fibers was less than 6.52%. The developed method was successfully applied to the preconcentration and determination of PAHs from environmental water samples. Furthermore the preparation of the ESS/AuNPs-S-C_{11}-OH fiber can be performed in a highly reproducible manner. This fabricated fiber exhibits high stability and withstands at least 200 extraction and desorption replicates.

Keywords: Au nanoparticles coating; Self-assembly; Stainless steel wire; Solid-phase microextraction; Polycyclic aromatic hydrocarbons

1. Introduction

Solid-phase microextraction (SPME) is an efficient solvent-free sample preparation technique which allows for integration of sampling, extraction, preconcentration and sample introduction in a single step [1]. Currently, SPME has aroused great interest in a broad field of analysis including environmental [2], food [3,4], pharmaceutical [5] and biological [6] samples due to its simplicity, rapidity, sensitivity and easy quantification. To date, commercially available SPME coatings are made from polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate (PA), carboxen (CAR) and polyethylene glycol (Carbowax, CW) in various thickness and combinations (PDMS/DVB, PDMS/CAR, CW/DVB) [7]. However, the fused silica supporting substrate is very fragile and thus must be handled with great care, which partly limits its service lifetime and widespread applications. Moreover the commercialized fiber coatings also have relatively low thermal stability, swelling in organic solvents and peeling off [8]. Therefore great effort has been devoted to the development of metal-based fibers such as aluminum [9,10], zinc [11], gold [12,13], silver [14], platinum [15], titanium [16-18], nitinol alloy [19,20], copper [21,22] and stainless steel (SS) wire [23-28]. These metal wires are mechanically strong and can be easily operated. Due to their quite different physicochemical properties from those of fused-silica fibers, a variety of preparation strategies of the metal wire supported SPME fibers were proposed.

Among the metal-based SPME fibers described, the SS wire was most commonly used as a supporting substrate with high mechanical and chemical stability, moderate elasticity and low cost. In particular, a new two-step process involving chemically etching procedure of SS wires and the post-fabrication of fiber coatings has proved very effective for the development of tightly attached coatings with unique structure [29,30]. According to this procedure, Liu et al rapidly prepared a robust Au particles coated fiber by direct chemical deposition onto an etched SS (ESS) wire for sensitive detection of PAHs [31]. These ESS wires proved to be promising alternative supporting substrates for subsequent fabrication of highly efficient fiber coatings because they exhibited good conductivity, rigidity and porous surface structure.

In recent years, special attention has been paid to coinage metal coatings and substrates due to their easy preparation and surface modification [25,31-34]. Organic molecules with thiol groups can be chemically bonded onto the surface of gold (Au) or silver (Ag) to form a self-assembled monolayer (SAM) [35]. In particular, Au nanoparticles (AuNPs) were immobilized on a SS wire layer by layer to prepare home-made SPME fibers for extraction of hydrophobic aromatic pollutants in rain and soil extracts [36]. The chemical and thermal stability as well as extraction selectivity based on the hydrophobic interaction and the electron-transfer effect between the π-donor system and the valency shell of Au enhanced its application. However, the layer-by-layer SAM process was cumbersome and time-consuming although the AuNPs coated fiber showed excellent properties. For this reason, AuNPs were attempted to directly deposit on an ESS wire by cyclic voltammetry and followed by surface modification of thiol compound via Au-S bonding. This approach proved to efficiently create a novel Au composite coating and greatly modify surface properties of AuNPs coating [37].

In this work, we described a new approach to the preparation of mercaptoundecanol (HS-C_{11}-OH) modified AuNPs coated the ESS (ESS/AuNPs-S-C_{11}-OH) fiber with direct chemical deposition of uniform AuNPs coating on the surface of the ESS wire followed by a self-assembly of mercaptoundecanol occurring uniquely on AuNPs coating. The extraction efficiency of this novel ESS/AuNPs-S-C_{11}-OH fiber was compared with that of commercial PDMS and PA fibers using polycyclic aromatic hydrocarbons (PAHs) as model compounds coupled to high-performance liquid chromatography with UV detection (HPLC-UV). Furthermore its extraction selectivity was evaluated for the concentration and separation of UV filters (UV), phthalic acid esters (PAEs) and PAHs. The microextraction conditions were investigated and optimized for the concentration and determination of PAHs. The SPME-HPLC-UV procedure with the ESS/AuNPs-S-C_{11}-OH fiber was established for selective concentration and determination of PAHs in environmental water samples.

2. Experimental

2.1 Materials and reagents

Chloroauric acid ($HAuCl_4 \cdot 4H_2O$) was purchased from Shenyang Chemical Reagents Company (Shenyang, China). Hydrofluoric acid (40%) was obtained from Shuangshuang Chemicals Co., Ltd, (Yantai, China). 11-Mercapto-1-undecanol ($HO\text{-}C_{11}\text{-}SH$) was obtained from Sigma-Aldrich (St. Louis, MO, USA). Sodium chloride (NaCl) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). HPLC-grade methanol was purchased from Yuwang Chemical Company (Yucheng, China). Certified individual standards of 2-hydroxy-4-methoxybenzophenone (BP-3), 2-ethylhexyl 4-methoxycinnamate (EHMC), 2-ethylhexyl 4-(*N,N*-dimethylamino) benzoate (OD-PABA), dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), di-*n*-octyl phthalate (DOP) and di-(2-ethylhexyl) phthalate (DEHP) were purchased from AccuStandard (New Haven, CT, USA). Certified 2-ethylhexyl salicylate (EHS) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). Certified individual standards of naphthalene (Nap), anthracene (Ant), phenanthrene (Phe), pyrene (Pyr) and benzo[a]pyrene (B[a]p) were purchased from Aldrich (St. Louis, MO, USA). Individual standard stock solutions were prepared in methanol at concentrations of 100 $mg \cdot L^{-1}$ and stored in the refrigerator at 4 ^{o}C, shielding from light. Working standard solutions were prepared by diluting the stock standard solution with ultrapure water to the required concentration to study extraction performance under different conditions. All chemical reagents were of analytical grade, unless otherwise stated. Stainless steel wire (75 mm × 0.20 mm O.D.) was obtained from Gaoge (Shanghai, China). A polydimethylsiloxane (PDMS) fiber (100 μm thickness) and a polyacrylate (PA) fiber (85 μm thickness) were obtained from Supelco (Bellefonte, PA, USA). 0.45 μm micropore membrane of polyvinylidene fluoride was supplied by Xingya Purifying Material Factory (Shanghai, China).

2.2 Apparatus

Chromatographic analyses were performed on a Waters 600E multi-solvent delivery system (Milford, MA, USA) equipped with a Waters 2487 dual λ absorbance detector and a zorbax Eclipse Plus C_{18} column (150 mm×4.6 mm, 5 μm, Agilent, USA). Data analysis was carried out using N2000 workstation software (Zhejiang University, China). Desorption was performed in a commercially available SPME-HPLC interface (Supelco, PA, USA). Ultrapure water was obtained from a Sudreli SDLA-B-X water purification system (Chongqing, China). Extraction was carried out in a DF-101S water bath with magnetic stirrer and a temperature-controlled system (Zhengzhou, China). Scanning electron microscopy (SEM) micrographs and surface composition of the fabricated fibers were obtained using an Ultra Plus microscope (Zeiss, Oberkochen, Germany) equipped with semi-quantitative microanalysis by energy dispersive X-ray spectroscopy (EDS).

2.3 Fabrication of ESS/AuNPs-S-C_{11}-OH fiber

One tip of the SS wire (1.5 cm) was firstly cleaned with acetone in ultrasonic bath for 5 min, followed by ultrapure water. Thereafter the SS wire was put into the HF solution (40%) for 50 min. After it was rinsed with ultrapure water in ultrasonic bath for 10 min, the etched SS (ESS) wire was dipped in a $HAuCl_4$ solution (0.06%w/w) for 4 h. Subsequently the fabricated ESS/AuNPs fiber was rinsed with water and dried in air. Before self-assembly, the ESS/AuNPs fiber was ultrasonically cleaned in ethanol for 0.5 min and immediately the ESS/AuNPs fiber was dipped into ethanol solution containing mercaptoundecanol of 0.1

mmol·L^{-1} for 24 h at room temperature. The excess mercaptoundecanol was removed through washing with ethanol and the ESS/AuNPs-S-C_{11}-OH fiber was dried in air. Finally the fabricated fiber was conditioned in the SPME-HPLC interface until the baseline was achieved.

2.4 Sample collection and pretreatment

Real water samples include 4 river water (pH~7.5), 1 wastewater (pH~7.8) and 1 snow water (pH~7.2) samples. River water samples were collected from different sites in the Lanzhou section of the Yellow River. A wastewater sample was collected from local wastewater treatment plant. A snow water sample was collected inside campus. All real water samples were collected in amber glass containers in November, 2014, filtered through 0.45 μm micropore membranes, and then stored in the dark at 4 ^{o}C.

2.5 SPME-HPLC procedure

The pH of sample solution or working standard solution was adjusted by sulfuric acid and sodium hydroxide. In a typical SPME procedure, a 10-mL of working standard solution or sample solution was added into a 20-mL glass vial with 1-cm magnetic stirrer bar inside and a Teflon septum. The ESS/AuNPs-S-C_{11}-OH fiber was exposed to the stirred sample solution for microextraction at elevated temperature. After extraction, the ESS/AuNPs-S-C_{11}-OH fiber was withdrawn from the vial and immediately introduced into the SPME-HPLC interface for static desorption in mobile-phase. The six-port valve was switched from load to inject position and the target analytes were introduced into the analytical column by mobile phase. The mobile phase consists of 88/12 (v/v), 75/25 (v/v) and 89/11 (v/v) methanol and water at a flow rate of 1 mL·min^{-1} for HPLC analysis of UV filters, PAEs and PAHs, respectively.

Corresponding wavelength of UV detection was set at 310 nm, 280 nm and 254 nm. Between two extractions, the fiber was immersed into methanol and ultrapure water for 15 min and 10 min to eliminate possible carry-over, respectively.

3. Results and discussion

3.1 Characterization of ESS/AuNPs-S-C_{11}-OH fiber

Surface morphology of the ESS/AuNPs-S-C_{11}-OH fiber was characterized by SEM. As compared with the untreated SS wire (Fig. 1a and 1b), the ESS wire exhibits a rough surface structure (Fig. 1c and 1d) and provides very large contact surface area for subsequent chemical deposition of AuNPs coating. As shown in Fig. 1e and 1f, a uniform AuNPs coating with cedar-like structure was grown onto the ESS substrate in a solution of $HAuCl_4$ at room temperature, different from those previously reported in the literatures [31,36]. Such a unique three-dimensional microstructure offers much larger surface area and more open access sites for subsequent self-assembly of mercaptoundecanol. As shown in Fig. 1g, the ESS/AuNPs-S-C_{11}-OH fiber appears to be more compact than the ESS/AuNPs fiber (Fig. 1e) after self-assembly. These characteristics are just desired for highly efficient extraction and fast mass transfer of the extracted analytes.

Fig. 1

The surface composition of the cedar-like AuNPs-S-C_{11}-OH coating was also analyzed by EDS. The surface spectrum obtained for the ESS wire shows peaks corresponding to the presence of Fe, Cr and Ni (Fig. 2a). For the cedar-like AuNPs coated ESS fiber, only the emission lines of Au appear (Fig. 2b), indicating that complete coverage of AuNPs coating deposited onto the surface of the ESS wire was achieved. Moreover corresponding EDS spectra of C, O and S were also observed for the ESS/AuNPs-S-C_{11}-OH fiber (Fig. 2c) except for those of Au. These EDS spectra clearly indicate that HS-C_{11}-OH molecules were self-assembled on the surface of AuNPs. This should be responsible for more dense morphology of the ESS/AuNPs-S-C_{11}-OH fiber.

Fig. 2

3.2 Extraction efficiency and selectivity

AuNPs coating exhibits good extraction capability for PAHs [31,36]. For this reason, the extraction performance of the ESS/AuNPs-S-C_{11}-OH fiber was evaluated by PAHs (Nap, Phe, Ant, Pyr and B[a]p) spiking water at the level of 25 $\mu g \cdot L^{-1}$ each analyte (Fig. 3b), and compared with that of commercially available 85-μm PA fiber (Fig. 3c) and 100-μm PDMS fiber (Fig. 3d) under the same conditions. Enhancement factors (EFs) of PAHs were estimated for ESS/AuNPs-S-C_{11}-OH, PDMS and PA fibers based on the ratio of chromatographic peak areas obtained by SPME-HPLC to those by direct HPLC for 10 μL of spiking water (Fig. 3a). As can be seen in Table 1, the ESS/AuNPs-S-C_{11}-OH fiber exhibits higher extraction efficiency for B[a]p, Pyr and Ant with lower solubility and larger molecular size than PDMS and PA which shows greater extraction capability for Nap and Phe. This result suggests that the AuNPs-S-C_{11}-OH composite coating should be hydrophobic in nature.

Fig. 3

The extraction efficiency and selectivity of the ESS/AuNPs-S-C_{11}-OH fiber was also comparatively studied for SPME of UV filters, PAHs and PAEs from aqueous phase. As compared with excellent extraction capability for PAHs (Fig. 4f) shown in Fig. 4, negligible extraction capability for UV filters (Fig. 4b) and no extraction capability for PAEs (Fig. 4d), were observed for the ESS/AuNPs-S-C_{11}-OH fiber. This result can be attributed to the hydrophobic interaction between PAHs and AuNPs-S-C_{11}-OH surface. Furthermore an electron transference between PAHs (π-donor system) and AuNPs coating may enhance the affinity beyond the hydrophobic effect [36]. B[a]p, Pyr and Ant with larger π-system should have improved affinity for AuNPs-S-C_{11}-OH composite coating. Thus the ESS/AuNPs-S-C_{11}-OH fiber gave greater extraction efficiency and better selectivity for B[a]p, Pyr and Ant. Indeed such an AuNPs-S-C_{11}-OH composite coating would exhibit good extraction efficiency for PAHs from complex environmental water samples. Therefore this novel fiber was attempted for selective SPME of B[a]p, Pyr, Ant, Phe and Nap in subsequent study.

Fig. 4

3.3 Optimization of SPME parameters

The adsorption and desorption of analytes on a SPME fiber is a dynamic equilibrium based on the partitioning of analytes between a fiber coating and the sample solution. They are subjected to several potential factors including extraction and desorption time, temperature, stirring rate and ionic strength. Thus the experimental conditions for SPME of B[a]p, Pyr, Ant, Phe and Nap were studied and optimized with working solutions at spiking level of 25 μg·L^{-1}.

3.3.1 Effect of extraction and desorption time

The amount of analytes extracted strongly depends on extraction time prior to extraction equilibrium. As a result, SPME was performed to examine the effect of extraction time from 10 to 60 min. As can be seen from Fig. 5a, the maximum extraction of PAHs was nearly achieved within 40 min. This result is clearly indicative of rapid mass transfer from bulk solution to the fiber coating due to much larger surface area of the ESS/AuNPs-S-C_{11}-OH fiber. Subsequent solvent desorption of the extracted PAHs was performed in mobile phase. The equilibrium of desorption was reached within 7 min. No carry-over of target analytes was detected for the second desorption. Thus, 40-min extraction and 7-min desorption were employed in subsequent experiment.

3.3.2 Effect of stirring rate

In SPME, stirring facilitates the mass transfer of analytes from the sample matrix into the fiber coating, which is favorable for the extraction equilibrium. Therefore the influence of stirring rate was examined from 100 r·min^{-1} to 600 r·min^{-1}. As shown in Fig. 5b, the best extraction efficiency of B[a]p, Pyr, Ant, Phe and Nap was almost achieved at the stirring rate of 500 r·min^{-1}.

Fig. 5

3.3.3 Effect of extraction temperature

Temperature has kinetic and thermodynamic effects on SPME and needs to be controlled precisely in SPME. Elevated temperature is favorable for the mass transfer of analytes from bulk phase to the fiber coating and shortens the equilibration time. On the contrary, it also reduces the distribution coefficients of analytes between the fiber coating and aqueous phase because surface adsorption is generally an exothermic process. In addition, higher temperature usually increases the solubility of analytes in aqueous phase and results in the decreased extraction efficiency accordingly. As shown in Fig. 5c, the best extraction efficiencies were achieved at 35 ^oC.

3.3.4 Effect of ionic strength

Salt addition is usually employed to decrease the solubility of analytes in the sample matrix, leading to higher extraction efficiency. Consequently, NaCl was deliberately added to maximize their extraction efficiency in SPME procedure. The extraction efficiency was monotonically decreased with the increasing concentration of NaCl. This may be due to the hydrogen bonding interaction between the hydroxyl moieties of sulfur anchoring undecanols and chloride ions [38], which is unfavorable for the adsorption of PAHs onto the the AuNPs-S-C_{11}-OH coating. In addition, it should be noted that addition of sodium chloride also leads to an increased viscosity of aqueous phase and thereby reduces the diffusion coefficients of target analytes in aqueous phase. Therefore, salt was not used in this study.

3.4 Analytical figures of merit

The proposed method was evaluated in terms of linearity range, correlation coefficient

(r^2), limit of detection (LOD), fiber repeatability and reproducibility under the optimized SPME conditions. The results are illustrated in Table 2. The LOD values were 0.010 μg·L^{-1} for B[a]p, 0.036 μg·L^{-1} for Pyr, 0.021 μg·L^{-1} for Ant, 0.044 μg·L^{-1} for Phe and 0.012 μg·L^{-1} for Nap at a signal-to-noise ratio of 3. The intra-day and inter-day relative standard deviations (RSDs) varied from 3.76% to 5.34% and from 4.22% to 5.53% for the single fiber repeatability for five replicate analyses at the spiking level of 25 μg·L^{-1}, respectively. The fiber-to-fiber reproducibility of five fabricated fibers in the same batch ranged from 5.15% to 6.52%. The fiber-to-fiber reproducibility of the prepared fibers among different batches was less than 7.32%.

3.5 Analysis of real samples

PAHs are a family of ubiquitous and persistent organic pollutants in environmental water [39]. They are of great concern because some PAHs are considered as potential carcinogens, and show tumorigenic activity and endocrine-disrupting activity in mammals [40]. Therefore the proposed method was employed for selective concentration and determination of PAHs in real environmental water samples. To evaluate accuracy and precision, water samples were fortified by spiking PAH standards into the real water samples at concentration levels of 10 μg·L^{-1} and 50 μg·L^{-1} before SPME, respectively. Fig. 6 exhibits representative chromatograms of direct HPLC for snow water (Fig. 6a) as well as corresponding SPME-HPLC with the ESS/AuNPs-S-C_{11}-OH fiber for snow water (Fig. 6b) and for spiking snow water (Fig. 6c). The results of three replicate analyses are listed in Table 3. The mean recoveries ranged from 94.50% to 107.5% and RSDs were between 3.26% and 5.86%. The matrix effect was minor. These experimental results show that the novel

ESS/AuNPs-S-C_{11}-OH fiber is effective and reliable for selective preconcentration and sensitive determination of trace target analytes in real environmental water samples.

Fig. 6

3.6 Stability and durability

The surface properties and the preparation strategies of the fiber coating plays a significant role in stability and durability of the SPME fiber and are very important for its practical applications. For this purpose, the stability of the ESS/AuNPs-S-C_{11}-OH fibers was examined by immersing in methanol, dimethylsulfoxide, tetrahydrofuran and chloroform overnight, respectively. The measured chromatographic peak areas of target analytes were decreased by less than 6.33% compared to their original ones for spiking water at the level of 25 $\mu g \cdot L^{-1}$. The fiber coating can also tolerate these organic solvents based on its SEM images. This result can be ascribed to the chemical stability of gold and strong Au-S bond. In this work, the ESS/AuNPs-S-C_{11}-OH fiber has withstood at least 180 times successive extraction and desorption runs according to the prescribed procedures and still maintains its extraction performance. The recovery from 98.66% to 102.4% was achieved for five replicate analyses of spiking water at the level of 25 $\mu g \cdot L^{-1}$. Furthermore, the ESS wire serves as a strong supporting substrate for the immobilization of the AuNPs-S-C_{11}-OH coating. The physical and chemical stability clearly demonstrates that the ESS/AuNPs-S-C_{11}-OH fiber will find its practical applications in environmental water samples.

3.7 Comparison of the proposed method with previous reports

The proposed method was compared with previously reported methods from the literature for the determination of PAHs. Table 4 summarizes their sample volume (V), extraction time (T), linear ranges, LODs, RSDs and recovery. It is found that the cedar-like AuNPs-S-C_{11}-OH coating allows for fast mass transfer from aqueous phase to the fiber coating due to its much larger surface area and more open access sites. Moreover the proposed method has the advantage of low LOD values for target analytes. The SPME procedure is simple, convenient, environmentally friendly and reliable for selective preconcnetration and sensitive determination of PAHs in real environmental water samples. The experimental results for the proposed method are comparable or better than those in the reported literatures [25,36,39,43].

4. Conclusions

In this study, the cedar-like AuNPs coating was fabricated on an ESS substrate by direct chemical deposition. Due to its unique nanostructure, the AuNPs coating has much larger surface area and more active sites for subsequent surface modification by self-assembly of mercaptoundecanol molecules. The ESS/AuNPs-S-C_{11}-OH fiber exhibits high extraction capability, good selectivity and fast mass transfer for SPME of target PAHs. In particular, it is more effective than the commercially available PDMS and PA fibers for SPME of B[a]p, Pyr and Ant with larger molecular size. The proposed SPME-HPLC method was employed to selectively extract and separate target PAHs in aqueous solution and very low LODs were obtained. Moreover the fabrication of the ESS/AuNPs-S-C_{11}-OH fiber was performed in a highly reproducible manner. In views of the chemical bonding of mercaptoundecanol to the AuNPs coating immobilized on the SS wire substrate, this novel ESS/AuNPs-S-C_{11}-OH fiber can be used for more than 180 extraction and desorption cycles without the loss of the extraction capacity. This fiber offered a simple, sensitive and inexpensive approach for selective concentration and determination of target PAHs in real environmental water samples. Furthermore the chemical deposition of AuNPs onto an ESS wire followed by self-assembly provides a promising alternative for reproducible preparation of stable, durable and inexpensive SPME fibers in the future.

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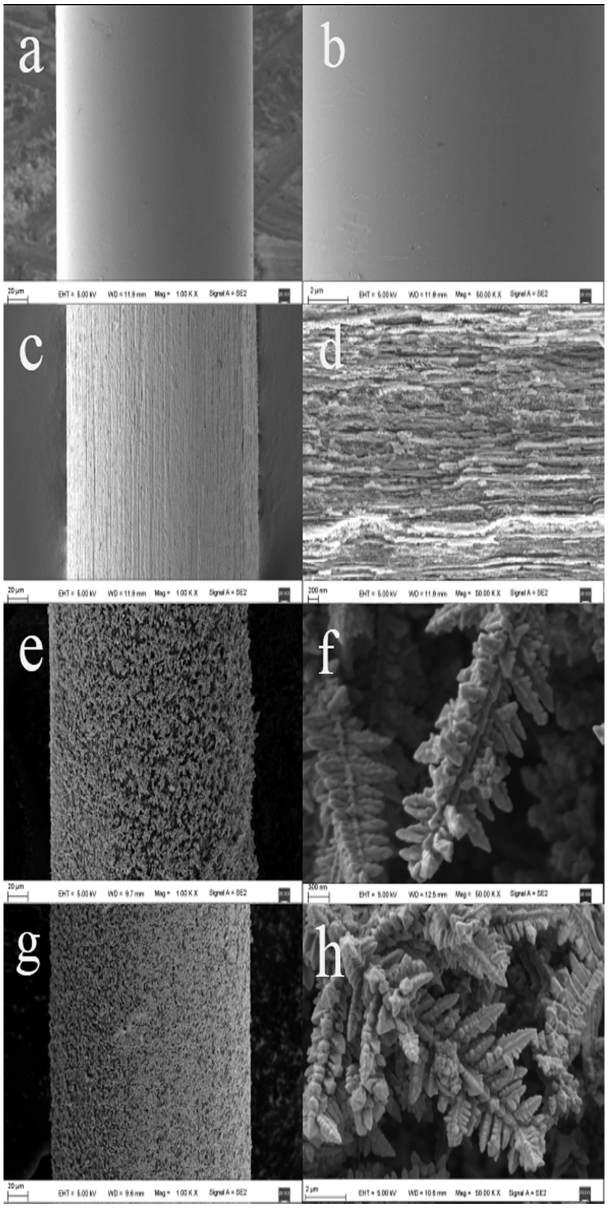

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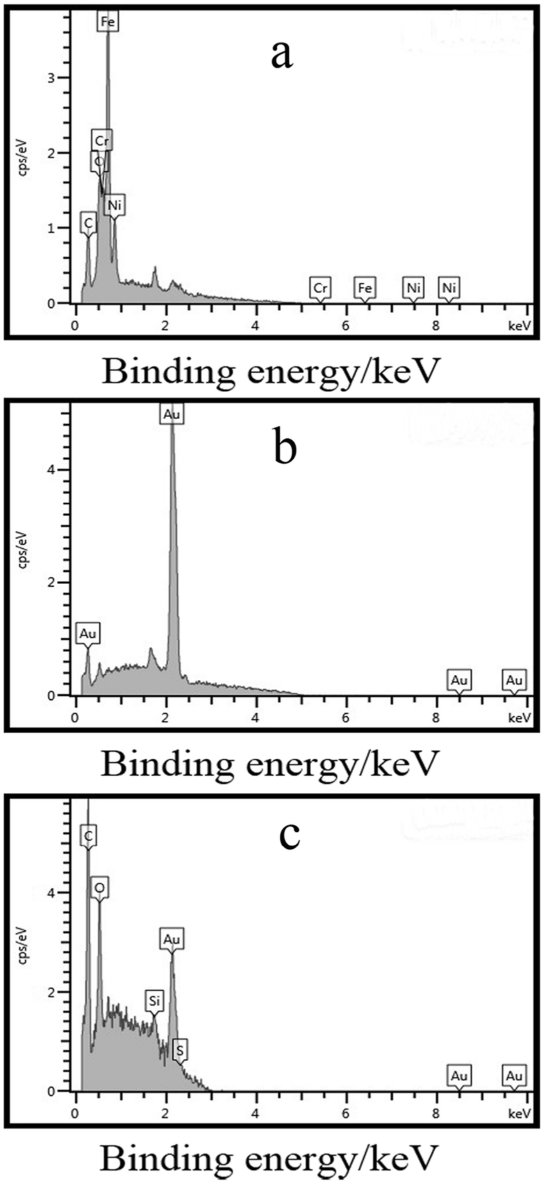

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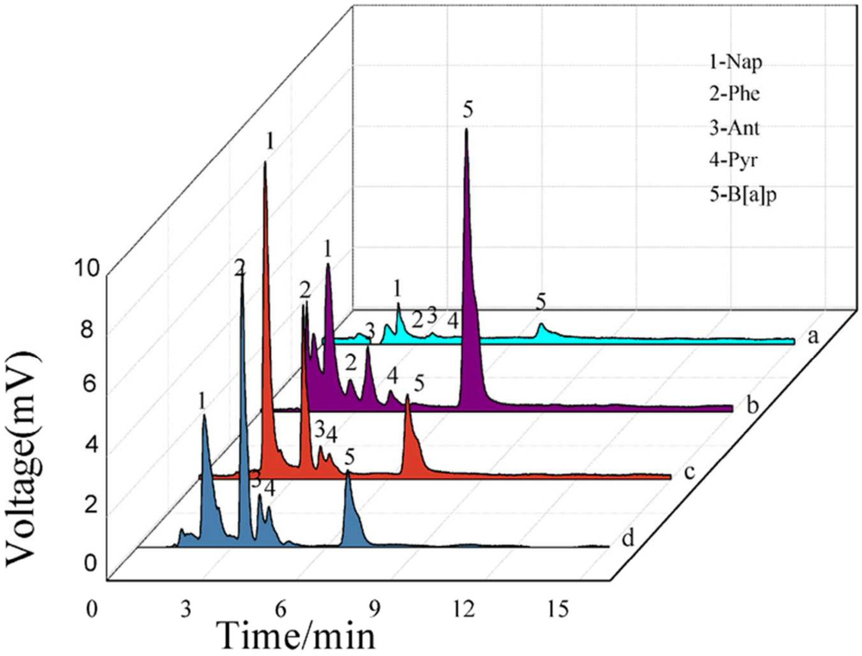

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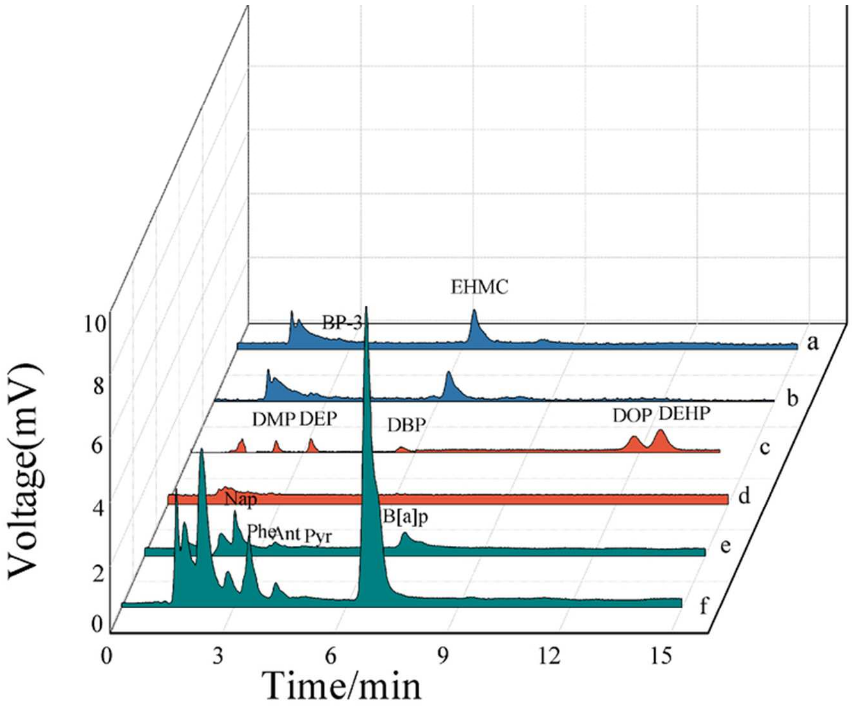

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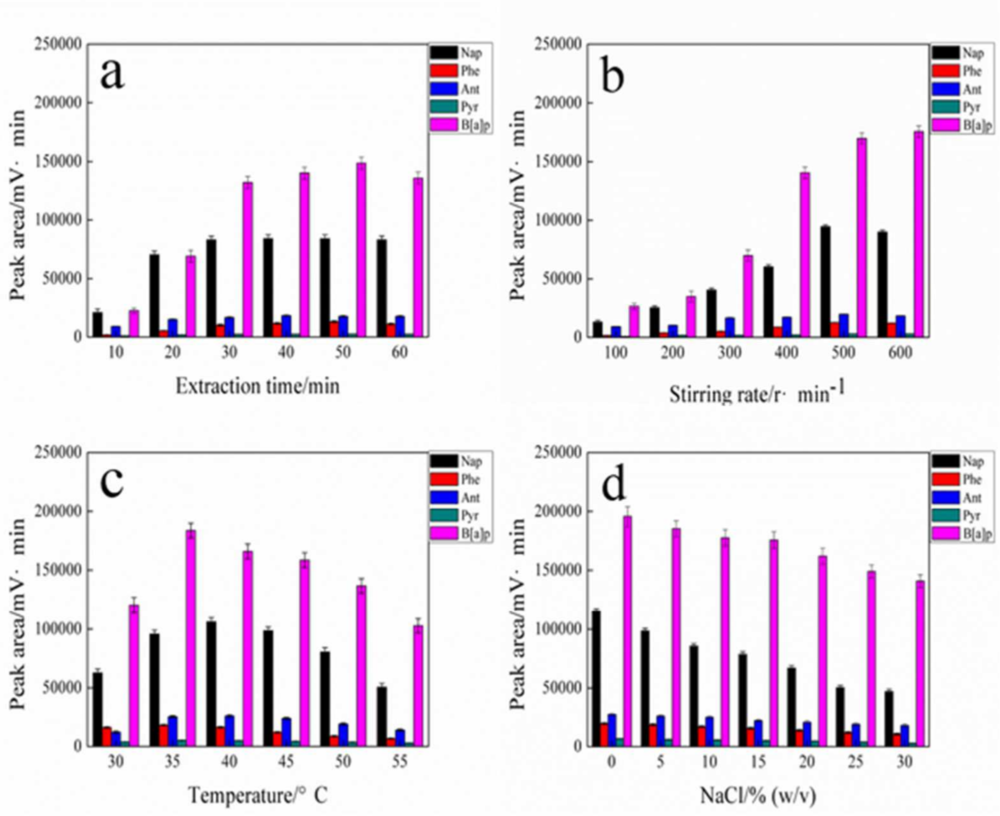

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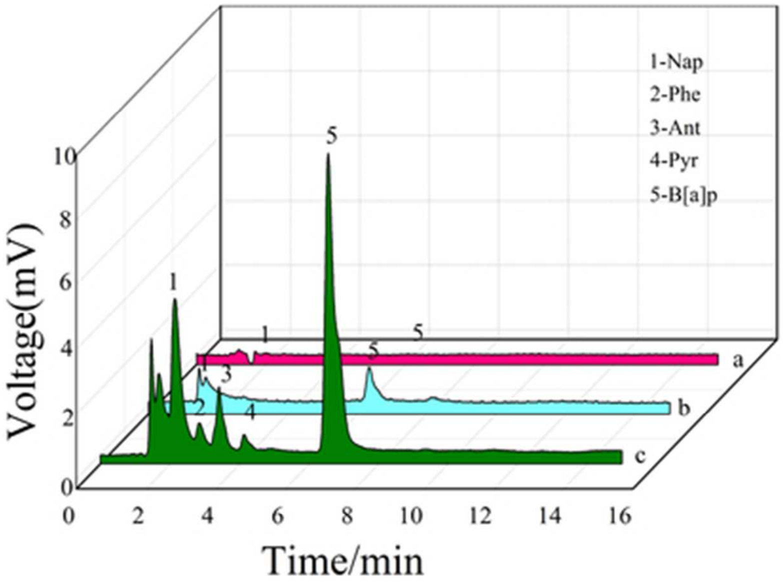

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Figure captions

Fig. 1. SEM images of the bare SS wire (a and b), the ESS wire (c and d), the ESS/AuNPs fiber (e and f) and the ESS/AuNPs-S-C_{11}-OH fiber (g and h) at low (×1000) and high (×50000) magnification.

Fig. 2. EDS spectra of the ESS fiber (a), the ESS/AuNPs fiber (b) and the ESS/AuNPs-S-C_{11}-OH fiber (c).

Fig. 3. Typical chromatograms of PAHs by direct HPLC (a), SPME-HPLC with the ESS/AuNPs-S-C_{11}-OH fiber (b), PA fiber (c) and PDMS fiber (d) for spiking water with 25·μg L^{-1} each analyte. Conditions: Extraction, 40 min; Desorption, 7 min; Temperature, 35 ^{o}C; Stirring, 500 r min^{-1}.

Fig. 4. Typical chromatograms of direct HPLC for UV filters (a), PAEs (c) and PAHs (e) as well as corresponding SPME-HPLC with the C_{11}-S-AuNPs/SS fiber for UV filters (b), PAEs (d) and PAHs (f) for spiked water with 25 μg·L^{-1} each analyte.

Fig. 5. Effect of extraction time (a), stirring (b), temperature (c) and ionic strength (d) on the extraction efficiency.

Fig. 6. Typical chromatograms of direct HPLC for snow water (a) as well as corresponding SPME-HPLC with the ESS/AuNPs-S-C_{11}-OH fiber for snow water (b) and for spiking snow

water with 25 $\mu g \cdot L^{-1}$ each analyte(c).

Table 1

EFs for each fiber toward each analyte

Analytes	EFs		
	ESS/AuNPs-S-C_{11}-OH	PDMS	PA
Nap	12.57	14.88	20.12
Phe	21.71	49.30	42.31
Ant	32.55	14.76	9.37
Pyr	25.96	26.59	19.13
B[a]p	28.34	19.35	18.20

Table 2

Analytical parameters of the proposed method (n=5)

PAHs	Linear range ($\mu g \cdot L^{-1}$)	r^2	Recovery (%)	Single fiber repeatability		Fiber-to-fiber reproducibility (%)	LOD ($\mu g \cdot L^{-1}$)	LOQ ($\mu g \cdot L^{-1}$)
				Intra-day (%)	Inter-day (%)			
Nap	0.05-300	0.9973	102.4	5.34	5.53	6.52	0.012	0.039
Phe	0.10-300	0.9983	98.67	4.72	4.88	5.15	0.044	0.145
Ant	0.10-300	0.9990	99.06	4.61	4.86	6.13	0.021	0.069
Pyr	0.10-300	0.9985	98.66	4.35	4.67	5.94	0.036	0.118
B[a]p	0.05-300	0.9992	101.24	3.76	4.22	5.32	0.010	0.032

Table 3

Analytical results of aromatic hydrocarbons in different environmental water samples (n=3)

Samples	PAHs	Original ($\mu g \cdot L^{-1}$)	Spiked with 10 $\mu g \cdot L^{-1}$			Spiked with 50 $\mu g \cdot L^{-1}$		
			Detected ($\mu g \cdot L^{-1}$)	Recovery (%)	RSD (%)	Detected ($\mu g \cdot L^{-1}$)	Recovery (%)	RSD (%)
River water under Bapanxia Bridge	Nap	1.20	12.04	107.5	4.65	52.38	102.3	5.34
	Phe	1.26	11.64	103.3	3.67	51.18	99.84	3.64
	Ant	ND [a]	9.87	98.70	4.29	49.91	99.88	5.03
	Pyr	ND	9.79	97.90	3.42	49.77	99.54	4.10
	B[a]p	1.12	11.06	98.75	3.27	51.39	105.2	3.84
River water under Yintan Bridge	Nap	1.89	12.58	105.8	5.40	53.11	102.3	5.29
	Phe	1.46	11.27	98.34	4.31	50.77	98.65	4.37
	Ant	1.28	11.30	100.1	3.66	51.07	99.59	4.27
	Pyr	ND	9.72	97.2	4.06	49.46	98.92	4.31
	B[a]p	2.24	12.56	102.6	3.49	52.88	101.2	3.36
River water Under Donggang Bridge	Nap	5.22	15.49	101.8	5.04	56.33	102.1	5.62
	Phe	4.26	15.07	105.7	4.51	55.62	102.5	4.85
	Ant	4.81	14.78	99.79	3.42	53.43	97.48	4.16
	Pyr	4.34	13.96	97.35	4.24	56.28	103.6	3.81
	B[a]p	5.64	15.37	98.27	3.55	57.72	103.7	4.10

River water under Shichuan Bridge	Nap	5.13	15.51	102.5	5.66	55.31	100.3	5.41
	Phe	4.03	13.82	98.50	4.68	52.61	97.37	4.55
	Ant	4.29	14.27	99.86	3.88	56.56	104.2	4.05
	Pyr	4.30	14.51	101.5	5.12	53.10	97.79	4.73
	B[a]p	5.31	16.26	106.2	4.63	55.96	101.2	4.55
Influent from wastewater treatment plant	Nap	4.31	14.77	103.2	5.86	54.91	101.1	5.44
	Phe	4.04	13.88	98.57	5.03	53.24	98.51	4.60
	Ant	3.85	13.66	98.62	4.73	53.51	99.36	4.16
	Pyr	3.27	12.60	94.50	5.26	51.14	96.00	5.34
	B[a]p	5.46	16.43	106.2	4.57	56.03	101.0	5.07
Snow water	Nap	1.32	12.04	106.4	4.86	51.85	101.3	4.33
	Phe	ND	9.72	97.20	4.22	48.95	97.90	3.95
	Ant	ND	9.63	96.30	3.37	48.22	96.44	3.26
	Pyr	ND	9.53	95.30	4.19	48.73	97.46	4.01
	B[a]p	1.04	11.73	106.2	4.35	52.15	102.2	3.94

[a] ND, Not detected or lower than LOD.

Table 4

Comparison of analytical data of the proposed method with previously reported methods

Methods	V (mL)	T (min)	Linear ranges (μg·L^{-1})	LODs (μg·L^{-1})	RSDs (%)	Recovery (%)	Refs
PDMS-SPME-GC-FID [a]	10	90	0.1-100	0.08-0.52	<19	–	[39]
PDMS-SPME-GC-MS	10	90	0.1-100	0.03-0.24	<19	69-105	[39]
PANI-SPME-GC-MS [b]	10	40	0.02-10	0.0001-0.006	8.80-16.8	82-111	[41]
PDMS/DVB-SPME -HPLC-FLU/UV [c]	15	60	0.04-15	0.005-0.027	0.97-2.21	81.23-89.11	[42]
AuNPs-SPME-GC-FID	20	50	0.05-300	0.025-0.25	2.49-7.90	78.4-119.9	[36]
AgMPs-SPME-GC-FID [d]	20	40	0.2-2000	0.02-0.1	3.20-6.30	82.3-93.9	[25]
AuMPs-SPME -HPLC-UV [e]	10	50	0.20-500	0.016-0.22	2.03-11.7	86.0-112.9	[43]
AuNPs-S-C$_{11}$-OH-SPME -HPLC-UV	10	40	0.05-300	0.010-0.044	3.36-5.86	94.50-107.5	Present method

[a] PDMS, polydimethylsiloxane; FID, flame ionization detection;

[b] PANI, polyaniline; MS, mass spectrometry;

[c] DVB, divinylbenzene; FLU, fluorescence;

[d] AgMPs, silver microparticles;

[e] AuMPs, gold microparticles;