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A novel TiO_2 nanotube array/Ti wire incorporated solid-phase microextraction fiber with high strength, efficiency and selectivity

Hongmei Liu [a,b], Daoai Wang [a,c], Li Ji [c], Jubai Li [a], Shujuan Liu [a], Xia Liu [a], Shengxiang Jiang [a,*]

[a] Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, No. 18 Tianshui Road, Lanzhou 730000, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[c] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

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ABSTRACT

A novel solid-phase microextraction (SPME) fiber is fabricated through the anodization of Ti wire substrates in an electrolyte containing ethylene glycol and NH_4F. By a combination of field emission scanning electron microscope and X-ray photoelectron spectroscope studies, it is shown that perpendicularly orientated and well-aligned TiO_2 nanotubes are grown *in situ* on the Ti wire substrate. The SPME fiber coupled with gas chromatograph (GC) is then used to extract polycyclic aromatic hydrocarbons (PAHs), anilines, phenols, and alkanes from standard and real water samples, and exhibits high selectivity for PAHs. After the optimization of adsorption factors (pH, ionic strength, time and temperature) and desorption factors (time and temperature) of the SPME fiber for PAHs, the limit of detection (LOD) of less than 0.1 $\mu g\,L^{-1}$ is achieved, and the calibration curves are all linear ($R^2 \geq 0.9898$) in the range from 0.1 to 1000 $\mu g\,L^{-1}$. Beyond that, the SPME fiber has high strength, large surface area, good stability at high temperature and in acid and alkali solutions, and long service life, making it have strong application potentials in the selective extraction of PAHs from complex samples at trace levels.

1. Introduction

Recently, a new extraction technology, SPME, is being developed and has attracted considerable attentions due to its high sensitivity, rapidity, simplicity and free of solvents. At present, this method has gained increasing industrial applications in trace analysis in many areas including environmental, food, and drug fields, but it also exhibits some drawbacks simultaneously. The core part of SPME technique is the SPME fiber consisting of a substrate fiber and a coating as a stationary phase to adsorb the analytes from samples. Almost all commercially available and new-type SPME substrate fibers are prepared with fused-silica, which is fragile and must be handled with great care, thus greatly limits the service life. Besides, many polymer coatings, such as carbowax/templated resin (CW–TPR), polydimethylsiloxane/divinylbenzene (PDMS–DVB), polyacrylate (PA), are commercially applied to extract many organic compounds [1–5]. However, polymeric coatings have a number of drawbacks including relatively low operating temperature (generally in the range of 240–280 °C), instability, less selectivity and swelling in organic solvents [6]. To overcome these problems, a number of high strength metal wires such as stainless steel wire [7–10], platinum wire [11–13], aluminum wire [14], gold wire [15], copper wire [16,17], zinc wire [18], titanium wire [19,20] and NiTi alloy [21–23] were selected as fiber substrate. Meanwhile, new-typed nanomaterial coatings were also introduced [24], which could not only overcome some shortcomings of commercial polymer coating materials, such as thermal instability, the stripping of coatings, but also possess some special properties, including large surface area and unique electronic and chemical properties.

Recent progress in the preparation of SPME fibers is being directed at the development of metal-based, unbreakable fibers with new coatings that have high sensitivity/selectivity for target analytes. In this paper, we introduce a new method in order to resolve these aspects. On one hand, the Ti metal wire instead of the friable fused-silica wire is adopted as the fiber substrate, which can provide high strength, and prolong the service life. On the other hand, perpendicularly orientated and well-aligned TiO_2 nanotube coating is successfully fabricated *in situ* on the Ti fiber substrate and used as the adsorptive phase. This unique nano-textured structure can greatly improve the surface area, and thus increase the enrichment effect. In addition, TiO_2, as a promising material, has gained great interest in analytical chemistry because of its good adsorptivity, durability, high stability, corrosion resistance, and non-toxicity, and has been successfully used as a stationary phase in high-performance liquid chromatography (HPLC) and solid phase

* Corresponding author. Tel.: +86 931 4968266; fax: +86 931 8277088.
E-mail address: sxjiang@lzb.ac.cn (S. Jiang).

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extraction (SPE) to analyze many chemicals [25–30]. Especially with the special relatively strong Lewis acidic and basic surface property, TiO_2 coatings would hold great prospects to exhibit special selectivity for extracting some compounds.

2. Experimental

2.1. Chemicals and reagents

Ti wire (⌀ 127 μm, 99.9% in purity) was obtained from the Alfa Aesar; naphthalene, anthracene, fluorene, and fluoranthene were purchased from the Shanghai Chemical Reagent Factory (Shanghai, China); *n*-nonane, *n*-decane, *n*-undecane, *n*-tridecane, and *n*-tetradecane were purchased from the Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China); phenol, *p*-chlorophenol, aniline, *p*-chloroaniline, and 1-naphthylamine were purchased from the Beijin Chemical Reagent Factory (Beijing, China); *p*-cresol, *m*-nitrophenol, 1-naphthol, *p*-nitroaniline, and *p*-toluidine were purchased from the Tianjin Chemical Reagent No. 1 Plant (Tianjin, China). All chemicals were of analytical grade.

The standard mixtures were divided into three groups: PAHs and alkanes the first group, phenols the second group and anilines the third group. All the standard mixtures were prepared by dissolving 10.0 mg of each compound in 10.0 mL of ethanol. The stock solution (1 mg mL^{-1}) was stored at 4 °C and diluted with ultrapure water to give the required concentration.

River water sample was collected from the Yellow River (Lanzhou, China). Wastewater (untreated) was sanitary wastewater in Lanzhou. All these samples were filtered through a 0.45 μm filter and stored (for two days) at 4 °C after collection.

2.2. Instruments

An Agilent 7890A series gas chromatograph (Agilent Technologies, USA) equipped with a flame ionic detector (FID) was used. The separation was carried out on an AT.SE-54 capillary column (30 m × 0.32 mm i.d. × 0.33 μm film thickness). Separation and detection parameters were optimized; for the first group, the column temperature was initially hold at 50 °C, and programmed at 5 °C min^{-1} to 300 °C, which was then held for 10 min; for the second group, the initial column temperature was hold at 80 °C, heated to 140 °C at 10 °C min^{-1}, then at the rate of 30 °C min^{-1} to 220 °C, finally programmed at 1 °C min^{-1} to 240 °C, which was then held for 5 min; for the third group, the initial column temperature was 100 °C, and programmed at 15 °C min^{-1} to 150 °C, then at the rate of 30 °C min^{-1} to 250 °C, finally programmed at 10 °C min^{-1} to 300 °C, which was then held for 5 min. Ultrapure nitrogen (>99.999%) was used as the carrier gas (1 mL min^{-1}) and the make-up gas (30 mL min^{-1}). The injector temperature was fixed at 300 °C, and the detector was fixed at 300 °C. The injection was performed in the split mode (1:1).

Scanning electron microscope micrographs of TiO_2 fibers were obtained on a field emission scanning electron microscope (FESEM, JSM-6701F, Japan).

The surface chemical composition of the fiber was determined on a PHI-5702 multifunctional X-ray photoelectron spectroscope (XPS, operated with an Al Kα radiation and the detecting chamber pressure of below 10^{-8} Torr).

2.3. Preparation of SPME fiber

Highly oriented TiO_2 nanotubes were prepared by a potentiostatic anodization method in a two-electrode electrochemical cell. In a typical process, the commercial Ti wire (99.9%) was used as a working electrode, and a graphite slice was served as a counter electrode. The Ti wire was thoroughly washed with ethanol, acetone and distilled water in sequence prior to the anodization. The wire was anodized at 20 V which were applied by a DC power supply (LW10J2, Shanghai) in an electrolyte containing ethylene glycol and 0.5 wt% NH_4F for 30 min at room temperature. After the anodization, the samples were washed with deionized water and then dried in air.

2.4. SPME

A modified 5 μL-syringe was used as an SPME device as described in Ref. [31]. A 8 μL stock solution was diluted with ultrapure water to 8 mL (1 μg mL^{-1}). After the homogenization, the needle of the SPME device was stuck through the septum of the vial containing the analytes. The sample was extracted through the direct immersion in the solution with a constant depth under the optimized time and temperature. The pH value and ionic strength were adjusted with HCl/NaOH and NaCl, respectively; a magnetic stirrer at a stirring rate of 600 rpm was used.

2.5. Test stability of coatings in acid, base solutions and under high temperature

The tip of the fiber was placed in two polytetrafluroethylene (PTFE) sealed vials loaded with hydrochloric acid (1×10^{-3} M) and sodium hydroxide (1×10^{-2} M) solution at room temperature, respectively. After 24 h, the fiber was taken out for the extraction experiment coupled with GC. The peak areas of analytes (1 μg mL^{-1}) before and after dipping into different solutions were compared. Then, the fiber was heated at 350 °C for 10 h, and the peak areas of analytes before and after heat treatment were also compared.

2.6. Determination of enhancement factors (EFs)

A 1 μL calibration solution spanning the concentration range from 1 to 1000 μg mL^{-1} was injected into the GC. A standard curve was then made by plotting the peak area *vs.* the concentration injected. The final concentration of the analyte after extracted from 1 μg mL^{-1} standard solution through the prepared TiO_2 nanotube fiber was calculated according to the standard curve. The EF was defined as the ratio of the final concentration to the original one.

3. Results and discussion

3.1. Preparation of TiO_2 SPME fibers

We have successfully prepared TiO_2 nanotubes with controllable pore size and length on Ti substrate by anodization in previous studies [32,33]. So the similar method was used to prepare TiO_2 nanotubes on Ti wires as the SPME fibers in present work. Fig. 1 shows the FESEM micrographs of the as-prepared SPME fiber with different magnification. It is seen that Ti wire surface after the anodization remains intact (Fig. 1(a) and (b)) and it consists of perpendicularly orientated nanotubes (Fig. 1(c)). The pore size and the length of the nanotubes are about 100 nm and 1 μm, respectively. XPS was carried out to evaluate the chemical composition of the film. Fig. 2 shows the Ti 2p and O 1s XPS spectra. Two Ti 2p peaks are observed at 469 and 464.7 eV, which can be assigned to the Ti $2p_{1/2}$ and Ti $2p_{3/2}$ binding energy of TiO_2 [34], indicating that Ti has been transformed to TiO_2 after the anodization. The same conclusion is also obtained from its O 1s XPS spectrum, which exhibits the main peak at 529.6 eV, which is ascribed to the oxygen atoms of TiO_2 [35] and an additional peak at 532.9 eV to the adsorbent oxygen (Fig. 2(b)). Combining the results of FESEM and XPS studies, we suggest that a perpendicularly orientated and well-aligned

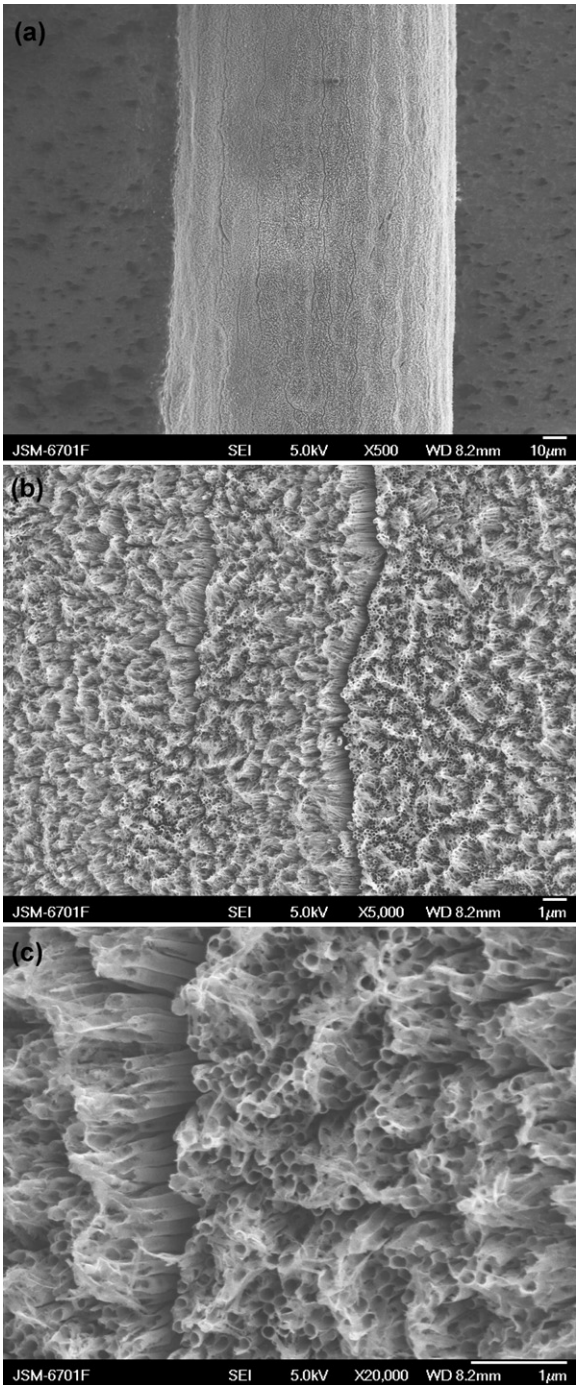

Fig. 1. FESEM images of TiO_2 nanotube array SPME fiber: (a) at a magnification of 500; (b) at a magnification of 5000; and (c) at a magnification of 20,000.

TiO_2 nanotube thin film has been successfully fabricated *in situ* on the Ti wire substrate.

3.2. Selectivity analysis

The as-prepared TiO_2 nanotube array/Ti wire SPME fiber coupled with GC was then used to extract four types of organic compounds, including PAHs (naphthalene, anthracene, fluorene, and fluoranthene), anilines (aniline, *p*-toluidine, *p*-chloroaniline, *p*-nitroaniline and 1-naphthylamine), phenols (phenol, *p*-cresol, *p*-chlorophenol, *m*-nitrophenol and 1-naphthol) and alkanes (*n*-nonane, *n*-decane, *n*-undecane, *n*-tridecane, and *n*-tetradecane)

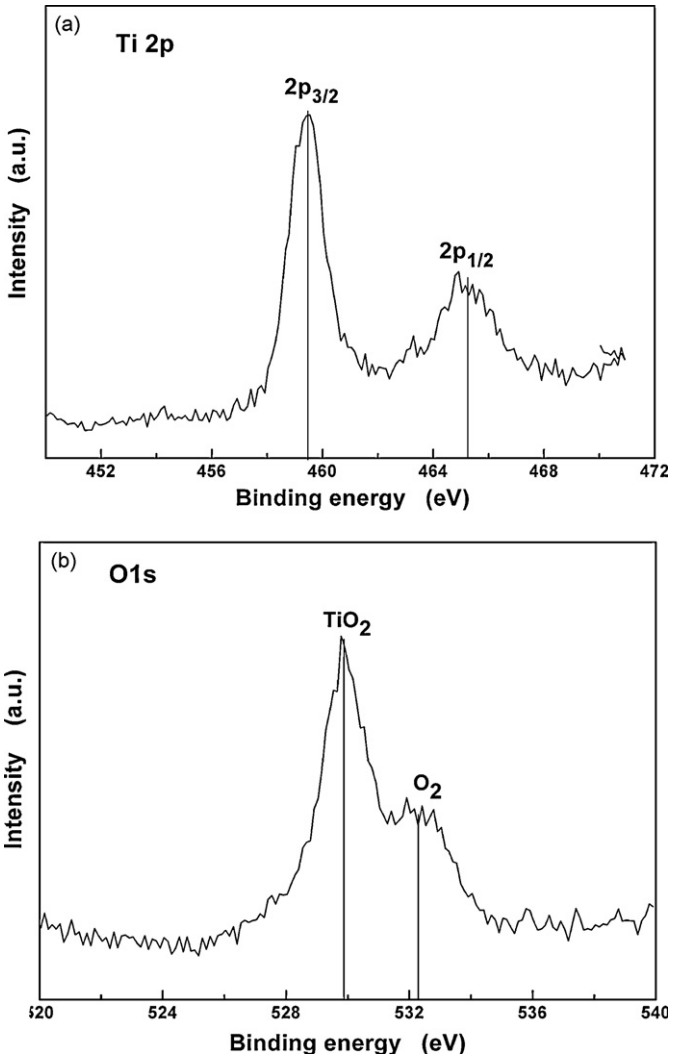

Fig. 2. XPS spectra of Ti wire surface after anodization: (a) Ti 2p and (b) O 1s.

from water samples. It is exciting that the fiber exhibits special extracting selectivity for PAHs and alkanes, while almost no extraction capability toward anilines and phenols as shown in Fig. 3. The same conclusion is also illuminated with the EF values of these compounds listed in Table 1. The EFs of PAHs reach 82.6–96.9, obviously larger than those of alkanes (39.4–45.3). While for the anilines and phenols, the EFs are almost zero. This result is also consistent with the performance of TiO_2 stationary phase in HPLC [25,26], where it shows short retention time and symmetrical peaks for basic compounds, and long retention time and poorly shaped peaks for acid compounds. This special selectivity may be attributed to the inherent chemical natures of TiO_2 sorbent coatings. On one hand, TiO_2 is an amphoteric material with the isoelectric point of 5, and so shows basic character in neutral aqueous solutions. Therefore, it excludes basic compounds, but strongly interacts with acidic compounds. The repulsive interaction makes the basic compounds (anilines) difficult to adsorb on the fiber, and the strong adsorption makes the acidic compounds (phenols) hardly desorb from the fiber. Thus, the fiber only exhibits SPME selectivity for the neutral compounds (alkanes and PAHs). On the other hand, the surface of TiO_2 nanotube fiber is of basic character in neutral aqueous solutions, which can be considered as electron donors, and PAHs have unsaturated and delocalized π molecular orbital, which can be considered as electron acceptors. Therefore, a special anion-π orbital (electron donor–acceptor) interaction is possibly in action during the SPME

Table 1
EFs and characteristic data of PAHs and alkanes using the established TiO_2 nanotube array, commercial and new-type SPME fibers coupled with GC.

Chemicals	EF	Linear range ($\mu g\,L^{-1}$)	Linearity/r^2	RSD (%)	LOD ($\mu g\,L^{-1}$)	LOD ($\mu g\,L^{-1}$) with commercial fiber [38]		Etched stainless steel wire [10]	
						PDMS	PA	Linear range ($\mu g\,L^{-1}$)	LOD ($\mu g\,L^{-1}$)
n-Nonane	39.4	–	–	–	–	–	–	–	–
n-Decane	45.7	–	–	–	–	–	–	–	–
n-Undecan	41.6	–	–	–	–	–	–	–	–
n-Tridecane	43.1	–	–	–	–	–	–	–	–
n-Tetradecane	40.2	–	–	–	–	–	–	–	–
Naphthalene	82.6	1–1000	0.9986	3.91	0.1	0.15	0.22	2.5–20	0.24
Fluorene	84.3	1–1000	0.9898	4.96	0.1	0.01	0.08	2.5–20	0.30
Anthracene	91.8	0.1–1000	0.9906	5.25	0.01	0.18	0.11	–	–
Fluoranthene	96.9	0.1–1000	0.9973	3.72	0.01	0.25	0.17	2.5–20	0.58
Phenols	0	–	–	–	–	–	–	–	–
Aniline	0	–	–	–	–	–	–	–	–

of PAHs using the TiO_2 nanotube array fiber. Furthermore, PAHs and alkanes are hydrophobic compounds, while phenols and anilines are hydrophilic, so it is easier for PAHs and alkanes than phenols and anilines to adsorb on the fiber. All these aspects contributed to the high extracting performance of PAHs than other compounds for the present TiO_2 nanotube array/Ti wire SPME fiber. As is known, PAHs are a widely distributed group of organic pollutants and are strongly mutagenic and/or carcinogenic, especially for those containing four or more aromatic rings, which have harmful biological effects on human health. The TiO_2 nanotube array/Ti wire SPME fiber just provides a hopeful approach to specifically extract and analyze trace amounts of PAHs from complex environment samples.

3.3. Optimization of SPME

The as-prepared TiO_2 nanotube array/Ti wire fiber coupled with GC was used for the SPME of alkane and PAH mixtures from water samples. To achieve the best extraction efficiency, effects of extracting parameters, such as the adsorption temperature and time, ionic strength of the solution, pH, and desorption conditions were systematically studied.

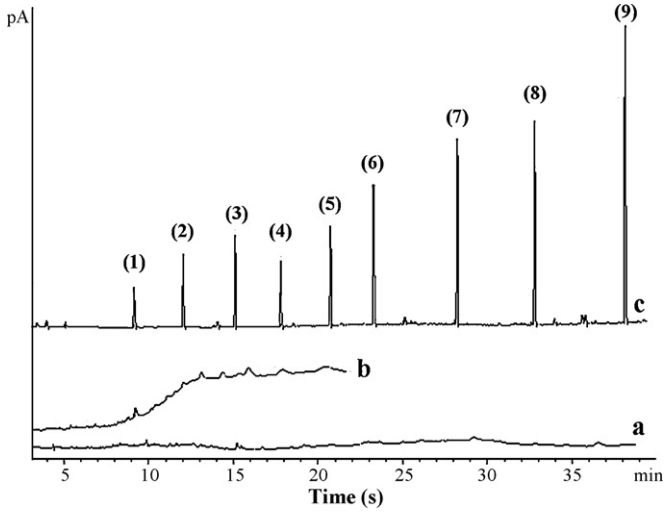

Fig. 3. Chromatograms of (a) phenols, (b) anilines, (c) PAHs and alkanes using the TiO_2 nanotube alignment SPME fiber coupled with GC. Concentration of each compounds: 1 $\mu g\,mL^{-1}$; NaCl: 0%; extraction time: 60 min; extraction temperature: room temperature; stirring rate: 600 rpm; and injection temperature: 300 °C. (1) *n*-nonane, (2) *n*-decane, (3) *n*-undecane, (4) *n*-tridecane,(5) *n*-tetradecane (6) naphthalene, (7) fluorene, (8) anthracene, and (9) fluoranthene.

3.3.1. Effect of extraction parameters

It is generally accepted that temperature has adverse effects on the extraction: on one hand, an elevated temperature can enhance the mobility of molecules and so quicken the extraction rate; on the other hand, it would decrease the distribution coefficient of analytes between the solid-phase coating and sample solution. Therefore, the selection of a proper temperature is necessary for the extraction process. In our experiments, the effects of the temperature on the extraction efficiency of analytes were studied in a range of 26–60 °C, as is shown in Fig. 4. The chromatographic peak areas reach the maximum for most compounds at 50 °C, and also keep the proper value for the other ones. So 50 °C was chosen for subsequent experiments.

It is known that the addition of a salt (NaCl) into a solution might either help with the extraction by the 'salt out effect' or deteriorate the extraction due to the competitive adsorption of Na^+ and Cl^-. The extraction efficiency as a function of salt concentration from 0% to 30% (30% is the saturated solubility of NaCl) was studied and shown in Fig. 5. It is found that with the increase of the salt concentration, chromatographic peak areas for the most analytes increase firstly up to 10% (w/v) salt concentration, indicating the 'salt out effect' plays a dominant role at the stage and then the peak areas decrease because of the competitive adsorption. Therefore, a concentration of 10% (w/v) was selected as the optimized salt concentration.

The pH value of the solution is another important factor for extraction. The effects of pH of the solution on the extraction

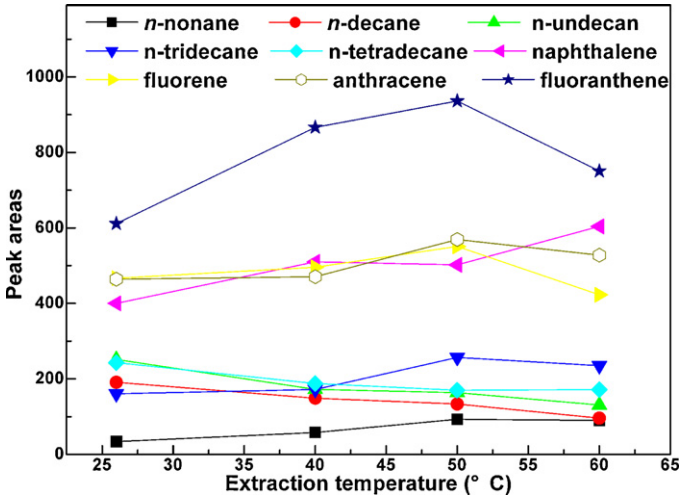

Fig. 4. Effect of extraction temperature on peak area of PAHs and alkanes. Extraction time: 60 min; NaCl: 0%; pH = 6.0; stirring rate: 600 rpm; desorption temperature: 300 °C; desorption time: 5 min; and sample concentration: 1 $\mu g\,mL^{-1}$.

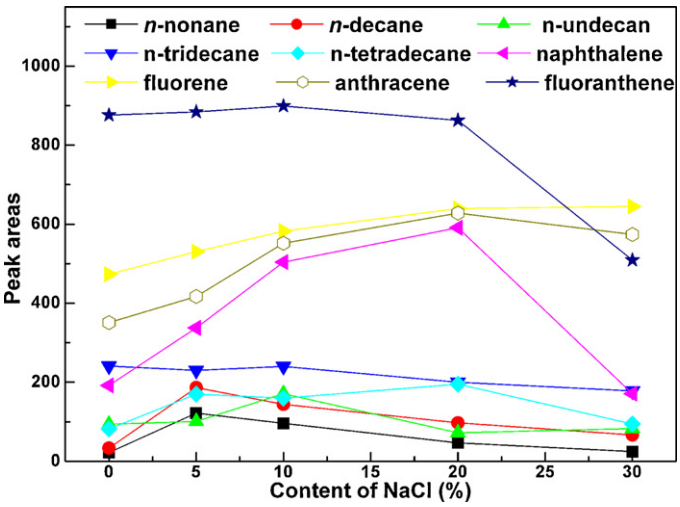

Fig. 5. Effect of ionic strength on peak area of PAHs and alkanes. Extraction time: 60 min; extraction temperature: 50 °C; pH = 6.0; stirring rate: 600 rpm; desorption temperature: 300 °C; desorption time: 5 min; and sample concentration: 1 μg mL^{-1}.

efficiency for these compounds were studied from 4 to 9. The extraction efficiencies of alkanes nearly have no differences for the tested pH levels, because the alkanes are nonpolar compounds that are always present as neutral form. For the PAHs, the extraction efficiencies increase with the increase of pH in the range of 4–6, and then decrease as pH increases further, but all the changes were little. The reason is that TiO_2 is an amphoteric material with the isoelectric point of 5, so it shows basic character in solutions of pH > 5. In this case, the special anion-π orbital (electron donor- acceptor) interaction between TiO_2 and PAHs can take actions and result in the better extraction efficiencies. On the other hand, when pH > 7, there exists an amount of OH^- anions in the solution, which can also interact with the PAHs and restrict the adsorption of PAHs on the fiber. Therefore, the optimal pH of the solution is 6 for the extraction of PAHs, and is adopted in our experiments.

Generally speaking, the extraction time is dependent on the equilibrium time of the analyte distribution between the fiber and samples. Long extraction time is advantageous to reach the best equilibrium translation. The extraction time profile of PAHs and alkanes is shown in Fig. 6. The amount of the extracted analytes (corresponding to the resulting peak areas) greatly increases as the

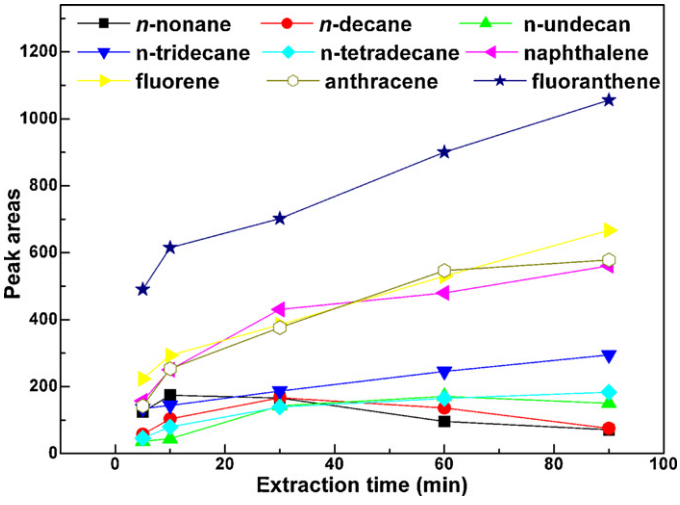

Fig. 6. Effect of extraction time on peak area of PAHs and alkanes. Extraction temperature: 50 °C; NaCl: 10%; pH = 6.0; stirring rate: 600 rpm; desorption temperature: 300 °C; desorption time: 5 min; and sample concentration: 1 μg mL^{-1}.

extraction time increases from 5 to 90 min, except for *n*-nonane, *n*-decane and *n*-undecane, which exhibit a little decrease as the extraction time increases from 60 to 90 min. This interesting phenomenon might be attributed to the competitive adsorption of the analytes. During the short extraction time, *n*-nonane, *n*-decane and *n*-undecane are easier to move to the surface of the TiO_2 nanotubes than PAHs due to the smaller molecular volume, and then adsorb on the fiber preferentially. With the increasing extraction time, more and more PAHs reach the surface of the TiO_2 nanotubes. Since the PAHs rather than alkanes have a stronger interaction with the TiO_2 nanotubes because of the special anion-π orbital (electron donor-acceptor) interaction, PAHs would substitute parts of the adsorbed *n*-nonane, *n*-decane and *n*-undecane on the fiber due to the competitive adsorption, and lead to a little decrease of their extraction efficiencies from 60 to 90 min. In fact, a 60-min extraction time is sufficient to achieve satisfactory extraction efficiency on the whole, although the equilibrium has not reached for most compounds. At the same time, with the consideration of the total operation time, the extraction time was set at 60 min.

3.3.2. *Effects of desorption parameters*

To reach the highest sensitivity, the desorption temperature and time were evaluated to ensure the complete desorption of anayltes from the fiber. The desorption temperature was evaluated at 240, 260, 280, 300 and 320 °C for 5 min. The results indicated that 300 °C was sufficient to achieve the complete desorption. Subsequently, evaluation of desorption time was carried out at 1, 3, 5 and 7 min. It is shown that the desorption was completed for all the test analytes at 300 °C for 5 min.

3.4. *Limit of detection, precision, accuracy and comparison with commercial SPME fibers*

The analytical parameters including the linearity, accuracy and precision, and limits of detection for the extraction of PAHs in ultrapure water with the TiO_2 nanotube array fiber are listed in Table 1. Under the optimized conditions, the linearity of this coated SPME–GC method was investigated with a serial of mixed standard solutions. The results indicated that all of them could be quantitatively determined within a wide range. As shown in Table 1, good linearities are achieved in the range of 0.1–1000 μg L^{-1} for anthracene and fluoranthene, 1–1000 μg L^{-1} for naphthalene and fluorene with satisfactory correlation coefficients. LODs for PAHs were determined by the gradual decrease of the concentrations of analytes until signals can just be detected at a signal-to-noise ratio of 3 (S/N = 3). LODs are 0.1 μg L^{-1} for naphthalene and fluorene, and 0.01 μg L^{-1} for anthracene and naphthalene. It is worth noticing that LODs of PAHs obtained by this fiber are comparable with, or even lower than those of the commercial fibers [36]. At the same time, this method exhibits wider linear ranges and lower LODs than the ones of hydrofluoric acid etched stainless steel wire fiber coupled with GC–FID, whose linear ranges are 2.5–20 μg L^{-1} and LODs are 0.24–0.58 μg L^{-1} for these four analytes (Table 1). Since the low LOD means a good detection capability for qualitative analysis and the wide linear range means a good detection capability for quantitative analysis, this TiO_2 nanotube array fiber is preponderant to extract and analyze PAHs at trace levels in environmental water samples with high sensitivity/efficiency.

3.5. *Application to real samples*

The established SPME–GC method was used to determine the contents of PAHs in Yellow River and sanitary wastewater samples with the TiO_2 nanotube array fiber, and the results are shown in Table 2. Anthracene and fluoranthene could be detected in the two samples and quantified in the wastewater, while fluorene

Table 2
Analytical results for the determination of PAHs in water samples ($n = 3$).

Compounds	Yellow River		Wastewater	
	No spiking	Recovery (RSD) % (spiked with 1 μg mL^{-1})	No spiking	Recovery (RSD) % (spiked with 1 μg mL^{-1})
Naphthalene	Not detected	78.57(±5.21)	Not detected	70.83(±6.34)
Fluorene	Detected but no quantified	116.03(±1.57)	Detected but no quantified	75.35(±3.21)
Anthracene	Detected but no quantified	86.54(±3.49)	4.72 μg L^{-1}	82.33(±7.59)
Fluoranthene	Detected but no quantified	119.28(±3.98)	2.98 μg L^{-1}	89.60(±6.48)

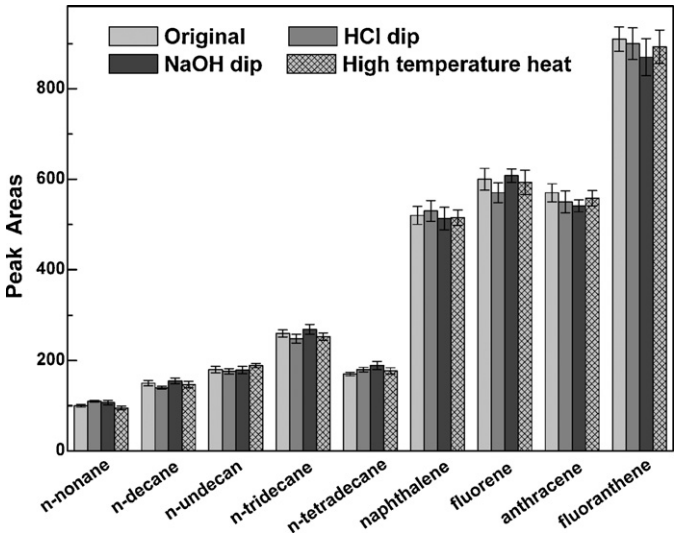

Fig. 7. Comparison of the chromatographic peak area of PAHs and alkanes before and after dipping the tip of the fiber into acid, basic solutions for 48 h, and treating it at high temperature (350 °C) for 10 h ($n = 3$).

could only be detected but not quantified in both the two samples. The concentration of anthracene and fluoranthene in the sanitary wastewater sample is found to be 4.72 and 2.98 μg L^{-1}, respectively. No naphthalene is detected in these two real water samples. The reason may be that naphthalene is biodegradable. In addition, For the sake of demonstrating the applicability and reliability, the recoveries of the target compounds are also determined. The recoveries are 78.57–119.28% for all the analytes in the Yellow River sample, and 70.83–89.60% in the sanitary wastewater sample.

3.6. Stability of the present fiber

The service life of coating is very important for practical applications. The damage of coating mainly occurs at the injection port of a gas chromatograph at high temperature and/or in acidic, alkali solutions in the matrix. Fig. 7 shows that the extraction abilities have no obvious deduction after the fiber is heated to 350 °C for 10 h, and dipped into hydrochloric acid (1×10^{-3} M) and sodium hydroxide (1×10^{-2} M) solution for 24 h. The relative standard deviations (RSDs) of extraction peak areas determined at a concentration of 1 μg mL^{-1} are less than 5%. All these merits greatly expand the application range of the present fiber toward high boiling-point compounds in strong acidic and alkali solutions, and also prolong the lifetime of the fiber for hundreds of times.

4. Conclusion

We demonstrate here a facile approach to fabricate SPME fiber of perpendicularly ordered TiO_2 nanotube arrays *in situ* on Ti wire substrates using the anodization method. The novel SPME fiber coupled with GC is then used to extract PAHs, alkanes, phenols and anilines from water samples, and exhibits many advantages over commercial SPME fibers, including high rigidity, long service life, good stability at high temperature and in acid and alkali solutions, large surface areas (high adsoptivity), good selectivity for PAHs, wide linear range and low LODs for extracting PAHs, simple preparation, and cost-effectiveness. The method represents a key addition to the family of SPME fibers, and has strong application potentials in the high-efficient and selective extraction of PAHs at trace levels from complex samples.

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