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In situ anodic growth of rod-like TiO_2 coating on a Ti wire as a selective solid-phase microextraction fiber

Yi Li [a], Mingguang Ma [a], Min Zhang [a], Yaoxia Yang [a], Xuemei Wang [a,b] Xinzhen Du [a,b*]

[a] College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

[b] Key Lab of Bioelectrochemistry & Environmental Analysis of Gansu, Lanzhou 730070, China

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[*] Corresponding author. Tel.: +86 931 7970796; fax: +86 931 7970796
E-mail address: duxz@nwnu.edu.cn (X.-Z. Du).

A novel rod-like TiO_2 based solid-phase microextraction (SPME) coating was directly fabricated by in-situ anodization of Ti wire substrates in ethylene glycol and aqueous solution with 5wt% NH_4F (v/v=1:1). The compact rod-like TiO_2 has much larger surface area with a diameter of about 150 nm and a length of about 1.2 μm. The SPME performance of as-fabricated fiber was investigated for the concentration and determination of polycyclic aromatic hydrocarbons, phthalates and ultraviolet (UV) filters coupled to high performance liquid chromatography with UV detection (HPLC-UV). It was found that the rod-like TiO_2 coating exhibited high extraction capability, good selectivity and rapid mass transfer for some UV filters. The main parameters affecting extraction performance were investigated and optimized. Under the optimized conditions, the calibration graphs were linear in the range of 0.05-200 $\mu g\cdot L^{-1}$. The limits of detection of the method were 0.024-0.032 $\mu g\cdot L^{-1}$ (S/N=3). The single fiber repeatability varied from 5.44% to 7.81% and the fiber-to-fiber reproducibility ranged from 7.41% to 8.63% for the extraction of spiked water with 50 $\mu g\cdot L^{-1}$ UV filters (n=5). The SPME-HPLC-UV method was successfully applied to the selective concentration and determination of target UV filters from real environmental water samples with recoveries from 84.68% to 104.8% at the spiking level of 5 $\mu g\cdot L^{-1}$, 25 $\mu g\cdot L^{-1}$ and 50 $\mu g\cdot L^{-1}$. The relative standard deviations were below 9.82%. Furthermore, the in situ growth of rod-like TiO_2 coating on a Ti wire by one-step anodization is simple, rapid and reproducible. The rod-like TiO_2 coating was cross-linked and embedded into the Ti wire substrate. As a result, the as-fabricated fiber is robust and has long service time.

Keywords: Rod-like TiO_2; Anodization; Solid-phase microextraction, Ultraviolet filters.

1. Introduction

Solid-phase microextraction (SPME) has been commonly used in analysis of trace organic contaminants since its introduction by Pawliszyn and co-workers in 1990s.[1] This technique is based on the partitioning of the organic analytes between the sample matrix and thin extraction coating deposited onto a fused silica fiber. Compared with other conventional techniques such as liquid-liquid extraction (LLE) and solid-phase extraction (SPE), SPME is a solvent-free technique by integrating sampling, isolation, enrichment and injection into one step and easily incorporated into chromatographic analyses.[2] Currently, commercially available sorbent coatings include polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB), carboxen (CAR), carbowax (CW) and their copolymers.[3,4] However, most of commercially available fibers are more expensive and also suffer from some drawbacks such as fragility, bending of the needle, the stripping of coatings, and easily swelling in organic solvents,[5] which limits their widespread applications. Therefore, the development of fiber coatings with excellent physical and chemical properties has attracted considerable research attention in the past two decades because it directly determines the sensitivity, selectivity, speed and robustness of a method. For these reasons, great efforts have directed to the development of metal-based fibers such as aluminum,[6] zinc,[7] gold,[8] silver,[9] platinum,[10] titanium,[11,12] nitinol alloy,[13,14] copper[15] and stainless steel wire.[16-19] These metal wire supported fibers are physically strong and can be handled with great convenience. Recently, new coating materials such as polyaniline, TiO_2/carbon nanotubes, and graphene were developed for SPME. These coating materials generally exhibit high extraction and good stability but inconspicuous selectivity. In contrast, inorganic nanostructures are promising alternatives for conventional SPME fibers owing to their well-defined structures with unique properties.

TiO_2 possesses some excellent characters such as no toxicity, high stability, good adsorption and biocompatibility,[20] and have attracted considerable attentions due to its fascinating structures and intriguing potential applications in photocatalysis,[21] photoelectrocatalysis,[22] gas sensors,[23] solar cells[24] and sensing devices[25]. Over the past years, many researchers take efforts to synthesize different dimensional TiO_2, including zero-dimensional nanoparticles,[26] one-dimensional nanotubes[27] and nanowires,[28] and two-dimensional nanosheets[29] by various techniques. Nanostructured TiO_2 was demonstrated to be excellent adsorbents for SPE of inorganic ions[30] and organic compounds.[31-33] However, only a few descriptions dealt with its SPME performance through controlling the nanostructure.[11,34,35] In situ fabrication of TiO_2-nanotubes coating on the surface of chemically oxidized Ti wire with hydrogen peroxide solution has been used for SPME of dichlorodiphenyltrichloroethane and its degradation products.[34] As the nanostructured TiO_2 was in situ formed on the surface of a Ti wire and chemically stable, this new SPME fiber exhibited long life span. Jiang and co-workers also fabricated a well-aligned TiO_2 nanotube arrays coated fiber through anodizing a Ti wire substrate for selective SPME of polycyclic aromatic hydrocarbons (PAHs).[35] Their adsorption strongly depends on morphology, structure and surface area of TiO_2. The diversity in nanostructure and adsorption affinity allows for elegantly designing TiO_2-based coatings to achieve high extraction capability and excellent separation for different analytes. However, up to now, there are no reports on rod-like TiO_2 as SPME fiber coatings.

In this study, we present a simple and rapid anodic method for the in situ fabrication of a novel fiber consisting of Ti wire coated with rod-like TiO_2 for the first time. Extraction capability and selectivity of the as-fabricated fiber were investigated for the concentration and determination of trace PAHs, phthalates (PAEs) and ultraviolet (UV) filters coupled with HPLC-UV. Finally, this novel rod-like TiO_2 coating was practically applied to the selective extraction of trace target UV filters from different environmental water samples. The SPME performance of this novel rod-like TiO_2 coated fiber was compared with that of commercial polydimethylsiloxane (PDMS) and polyacrylate (PA) fibers under the optimized conditions.

2. Experimental

2.1 Chemicals and reagents

Ti wire (purity 99.9%, ϕ0.25 mm) was obtained from Alfa Aesar (Ward Hill, MA, USA). 0.45 μm micropore membrane of polyvinylidene fluoride was supplied by Xingya Purifying Material Factory (Shanghai, China). Ammonium fluoride (NH_4F) and ethylene glycol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The HPLC-grade methanol was purchased from Yuwang Chemical Company (Shandong, China). Sodium chloride (NaCl) was obtained from Shanghai Hunter Fine Chemicals Ltd (Shanghai, China). Certified individual standards of naphthalene (Nap), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu) and pyrene (Pye) were purchased from Aldrich (St. Louis, MO, USA). Certified individual standards of dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), di-n-octyl phthalate (DOP), di-(2-ethylhexyl) phthalate (DEHP), 2-hydroxy-4-methoxybenzophenone (BP-3), 2-ethylhexyl 4-methoxycinnamate (EHMC) and 2-ethylhexyl 4-(*N,N*-dimethylamino) benzoate (OD-PABA) were purchased from AccuStandard (New Haven, CT, USA). 2-Ethylhexyl salicylate (EHS) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). The stock standard solution of 100 $mg \cdot L^{-1}$ of each compound was prepared in methanol and stored in amber bottles 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 other reagents were of analytical grade.

2.2 Instruments

HPLC measurements 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 C18 column (150 mm×4.6 mm, 5 μm, Agilent, USA). Data collection was obtained with a N2000 workstation (Zhejiang University, China). Desorption was performed in a commercially available SPME-HPLC interface (Supelco, PA, USA) and sealed by polyether ether ketone septum which is tight enough to withstand pressure as high as 29.7 MPa. Ultrapure water was obtained from a Sudreli SDLA-B-X water purification system (Chongqing, China). Heating and stirring was carried out in a DF-101S water bath with magnetic stirrer (Changcheng, Zhengzhou, China). Electrochemical anodization was carried out on a JWD-12.2 precise power supply (Shanghai, China). The morphology and composition of the fabricated fibers were characterized by an Ultra Plus microscope (Zeiss, Oberkochen, Germany) with semi-quantitative microanalysis by energy dispersive X-ray spectroscopy (EDS). The crystallinity of the rod-like TiO_2 coating was characterized by a

LabX XRD-6100 X-ray diffractometer (Shimadzu, Tokyo, Japan).

2.3 Fabrication of rod-like TiO_2 coated fibers

Rod-like TiO_2 coating on the surface of the Ti wire was in situ frabricated by a one-step anodization method in a mixture of ethylene glycol and aqueous solution with 5wt% NH_4F (v/v=1:1). Prior to anodization, the Ti wire was thoroughly washed with acetone and ultrapure water in an ultrasonic bath. The anodization was performed at a controlled potential of 20 V for 45 min at 35 ^{o}C in a two-electrode configuration with a Ti wire as the working electrode and a platinum rod as the counter electrode. After anodization, the as-fabricated fibers were gently rinsed with ultrapure water and then dried in air.

2.4 SPME-HPLC procedure

The extraction was carried out with 15 mL of working standard solution or sample solution in a 20-mL glass vial. The pH of sample solution was adjusted to 7.0 prior to extraction. The as-fabricated fiber was directly immersed into the stirred solution for a period of time at elevated temperature. After extraction, the fiber was withdrawn from the sample solution and subsequently introduced into the SPME-HPLC interface for static desorption in mobile-phase. After solvent desorption, six-port valve was switched from load to inject position, the mobile phase was passed through the interface and target analytes were introduced into the analytical column. Separation and detection parameters were optimized. The mobile phase was methanol/water of 90/10 (v/v), 75/25 (v/v) and 86/14 (v/v) at a flow rate of 1 $mL \cdot min^{-1}$ for HPLC analysis of PAHs, PAEs and UV filters, respectively. Corresponding wavelength of UV detection was set at 254 nm, 280 nm and 310 nm. Between two extractions, the fiber was immersed into methanol and ultrapure water to eliminate possible carry-over for 10 min and 5 min, respectively.

3. Results and discussion

3.1 Characterization of rod-like TiO_2 coated fiber

Figure 1 shows scanning electron microscopy (SEM) images of bare Ti wire and the as-prepared fiber. It can be seen from the low magnification image (Figure 1b) that the coating is even and almost covers the whole Ti wire and as-fabricated fiber exhibits the randomly oriented rod-like coatings after electrochemical anodization (Figures 1c and 1d) compared with smooth bare Ti wire (Figure 1a). The cross section view and side view (Figures. 1e and 1f) show the compact rod-like TiO_2 coating on the anodized Ti wire were formed with a diameter of about 150 nm and a length of about 1.2 μm. As shown in Figure $1b_1$ (inset), the obtained EDS spectrum clearly indicates peaks corresponding to the presence of titanium and oxygen. Figure 2 is an x-ray diffraction profile of the rod-like TiO_2 coating prepared by in-situ anodization. Obviously, an amorphous phase is dominant. This profile is similar to that reported by Quan et al.[36] Furthermore these rod-like TiO_2 coatings were cross-linked and tightly embedded into the Ti wire substrate. This unique structure possesses much larger surface area, more open access sites and better durability, which are most desirable for highly efficient SPME.

Figure 1

Figure 2

3.2 Dependence of the rod-like TiO_2 coating on anodic time

The extraction capability of a fiber coating material greatly depends on its structure and surface area. For this purpose, dependence of the rod-like TiO_2 coating on anodic oxidation time was further investigated. Figure 3 shows SEM images of some fibers fabricated within anodic time of 30 min, 45 min, 60 min and 90 min. The fabricated rod-like TiO_2 coating is compact and uniform with the length of about 1.0 μm, 1.2 μm, 1.6 μm and 3.0 μm respectively. Figure 4 exhibits corresponding chromatograms for SPME-HPLC procedure with the as-fabricated fibers. The best extraction efficiency of OD-PABA, EHMC and EHS was achieved for the Ti wire anodized within 45 min. This result suggests that such rod-like TiO_2 structure should significantly increase available surface area of the as-fabricated fiber and thereby enhance its extraction efficiency of UV filters. Therefore, 45 min was employed as a reasonable compromise between good sensitivity and an acceptable time for the in situ fabrication of the rod-like TiO_2 coating in subsequent experiment.

Figure 3

Figure 4

3.3 Extraction selectivity of rod-like TiO_2 coated fiber

The extraction selectivity of the rod-like TiO_2 coated fiber was further studied for SPME of non-polar PAHs (Nap, Phe, Ant, Flu and Pyr), different polar PAEs (DMP, DEP, DBP, DOP and DEHP) and less polar UV filters (BP-3, OD-PABA, EHMC and EHS) from water phase. The as-fabricated fiber exhibits excellent extraction selectivity for OD-PABA, EHMC and EHS, while almost no extraction capability toward PAHs, PAEs, and BP-3 as shown in Figure 5. This result may be attributed to the inherent physicochemical nature of rod-like TiO_2 coatings. On the one hand, the as-fabricated fiber exhibits good affinity for organic compounds with polar functional group due to the presence of Ti-OH at the surface of TiO_2 coating. On the other hand, it is expected that strong Lewis acidic sites at the surface of TiO_2 would show strong affinity for OD-PABA, EHMC and EHS with Lewis basic character. As a result, the as-fabricated fiber shows good selectivity for the extraction of OD-PABA, EHMC and EHS. Such a TiO_2 structure provides a potential approach to selective extraction of OD-PABA, EHMC and EHS from complex environment water samples and greatly enhances their extraction efficiency.

Figure 5

3.4 Optimization of SPME conditions

In the present study, one of the main goals is to develop SPME-HPLC-UV method for the analysis of OD-PABA, EHMC and EHS in aqueous samples. Hence, several potential factors including extraction and desorption time, temperature, stirring rate and ionic strength were studied and optimized with working solution at spiking level of 50 $\mu g \cdot L^{-1}$.

3.4.1 Effect of extraction and desorption time

Extraction time and desorption time are very important parameters not only to ensure the high sensitivity and good reproducibility, but also to avoid the cross-over contamination between different analyses. Figure 6a shows the extraction time profile of OD-PABA, EHMC and EHS. The equilibration time clearly indicates that the rod-like TiO_2 coating is favorable for their mass transfer from bulk solution to fiber coating. 30 min was needed to nearly reach the equilibrium between the rod-like TiO_2 coating and aqueous phase. Thereafter solvent desorption of the extracted UV filters was performed in mobile phase. For target UV filters, constant desorption maximum was achieved within 4 min. Thus extraction of 30 min and desorption of 4 min were employed in subsequent experiment.

Figure 6

3.4.2 Effect of extraction temperature

The extraction temperature is another important parameter to be controlled. It is generally accepted that high temperature is favorable to mass transfer from aqueous phase to fiber coatings. Figure 6b exhibits the effect of temperature on the extraction of OD-PABA, EHMC and EHS from 15 to 65 ^{o}C. The highest extraction efficiencies were achieved at 35 ^{o}C. In this case, the kinetics controlled adsorption is predominant. Subsequently, the extraction capability decreased when the temperature continuously increased. This result can be ascribed to their decreased distribution coefficients between the rod-like TiO_2 coating and aqueous phase at elevated temperature because adsorption interaction is generally an exothermic process.[37] In addition, the increased solubility of target UV filters also results in decreased extraction efficiency at higher temperature. Therefore 35 ^{o}C was used for extraction in the study.

3.4.3 Effect of salt

Addition of salt usually decreases the solubility of organic compounds in aqueous phase due to salting-out effect and thereby enhances their partitioning coefficients to fiber coating. Thus effect of salt was examined by addition of NaCl into the working solutions. As shown in Figure 6c, the best extraction efficiencies of OD-PABA, EHMC and EHS were observed in aqueous phase with NaCl of 5% (w/v). In this case, the salting-out effect plays a major role. At higher concentration than 5%, the competitive effect may occur due to the Lewis acid-base interaction between the TiO_2 coating and chloride ions,[38] and thereby result in decreased extraction efficiencies. Moreover, more salt addition also leads to an increase in sample viscosity and brings about a negative effect on the extraction. Therefore, NaCl of 5% was selected in this study.

3.4.4 Effect of stirring rate

In general, extraction efficiency enhances with increasing stirring rate because of accelerated diffusion of analytes in solution. In this study, the extraction efficiency maximum of OD-PABA, EHMC and EHS was achieved at the stirring rate of 800 $r\cdot min^{-1}$. Thereafter, more vigorously stirring might lead to tiny bubble formation which is unfavorable to the adsorption of analytes molecules onto the surface of the rod-like TiO_2 coating. Therefore the stirring rate was fixed at 800 $r\cdot min^{-1}$ in the experiment.

3.5 Analytical performance

The analytical performance of the rod-like TiO_2 coated fiber was examined for target UV filters under optimized conditions. Table 1 summarizes their linear ranges with corresponding correlation coefficients (r^2), recoveries and limits of detection (LOD) (S/N = 3) of the proposed method. The rod-like TiO_2 coated fiber exhibited wide linearity with 4 orders of magnitude for target UV filters. The single fiber repeatability for five replicate extractions of UV filters at the spiking level of 50 $\mu g \cdot L^{-1}$ varied from 5.44% to 7.21% and from 5.71% to 7.81% for intraday and interday SPME-HPLC of UV filters, respectively. The fiber-to-fiber reproducibility of five parallel fabricated fibers ranged from 7.41% to 8.63% under the same conditions.

3.6 Real samples analysis

UV filters are synthetic chemicals and widely used in sunscreen, cosmetics and personal care products in order to protect human skin from direct sunlight exposure by absorbing UV radiation.[39] Their detection has shown that UV filters are directly or indirectly released into aquatic environment during bathing and washing activities via domestic wastewater.[40] A preliminary study reported that some UV filters are estrogenic, antiestrogenic, androgenic and antiandrogenic in vitro and in vivo.[41] Therefore real water samples were freshly collected from different sites in the Lanzhou section of the Yellow River and from local wastewater treatment plant. The proposed method was employed for the preconcentration and determination of targeted UV filters in real environmental water samples. Figure 7 shows typical chromatograms of direct HPLC (Figure 7a) and SPME-HPLC with the rod-like TiO_2 coated fiber for raw and spiked river water under Bapanxia Bridge (Figure 7b-e). The matrix effect was negligible. As compared with commercially available 100 μm PDMS (Figure 7f) and 85 μm PA fibers (Figure 7g), the rod-like TiO_2 coated fiber (Figure 7e) exhibits greatest extraction capability of target UV filters. For raw and spiked environmental water with 5 $\mu g \cdot L^{-1}$, 25 $\mu g \cdot L^{-1}$ and 50 $\mu g \cdot L^{-1}$ of UV filters, the analytical results of three replicate analyses were listed in Table 2, respectively. The mean recoveries ranged from 84.68% to 104.8% and RSD was between 6.41% and 9.82%. These experimental data clearly demonstrate that the novel rod-like TiO_2 coated fiber is reliable and suitable for the preconcentration and determination of trace target UV filters in environmental water samples.

Figure 7

3.7 Stability and durability

Generally, the commercially available SPME fibers with polymeric coatings suffer from swelling in organic solvents in immersion mode.[5] For this reason, the stability of the rod-like TiO_2 coatings was examined after exposure to methanol, dimethylsulfoxide, tetrahydrofuran and chloroform for 48 h, respectively. The rod-like TiO_2 coated fiber is stable and can not suffer from any damage in these organic solvents based on its SEM images. In the experiment, the rod-like TiO_2 coated fiber has withstood at least 250 times successive extraction and desorption runs in mobile phase according to the prescribed experimental procedures. The recovery from 92.4% to 105.4% was also obtained for three replicate analyses of spiked water with 50 $\mu g \cdot L^{-1}$. Furthermore, this fiber is still reusable after two week storage, indicating that the rod-like TiO_2 coating was tightly attached to the Ti wire substrate. Its mechanical and chemical stability clearly demonstrate that the rod-like TiO_2 coated fiber will find its practical applications in environmental water analysis.

4. Conclusion

In this study, a novel rod-like TiO_2 coated fiber was directly fabricated on a Ti wire substrate by simple one-step anodization in a highly reproducible manner and its SPME performance was studied in detail. Due to its unique structure, the rod-like TiO_2 coating has much larger surface area and open access sites for adsorption of target analytes and exhibits high extraction capability, good selectivity and fast mass transfer for SPME of OD-PABA, EHMC and EHS. Furthermore the as-fabricated fiber is more effective than the commercially available PDMS and PA fibers for SPME of target UV filters. In addition, the rod-like TiO_2 were embedded into the Ti wire substrate. Due to the inherent chemical stability of the rod-like TiO_2 coating and the mechanical durability of the Ti wire substrate, this novel rod-like TiO_2 coated fiber is stable and durable. SPME with rod-like TiO_2 coating in combination with HPLC-UV provided a simple, fast, highly sensitive and reproducible method for selective concentration and determination of target UV filters from environmental water samples.

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Graphical abstract

A novel rod-like TiO_2 based solid-phase microextraction (SPME) coating was directly fabricated by in-situ anodization of Ti wire substrates in ethylene glycol and aqueous solution with 5wt% NH_4F (v/v=1:1). The compact rod-like TiO_2 has much larger surface area with a diameter of about 150 nm and a length of about 1.2 μm. (Fig. 1). It has larger surface area and longer service time for sensitive determination of ultraviolet filters in environmental water samples.

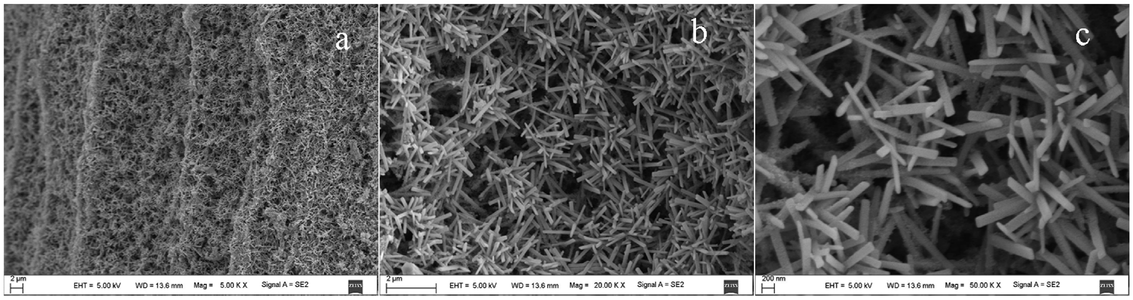

Figure 1. SEM images of the rod-like TiO_2 coated fiber (a×5000, b× 20000 and 50000).

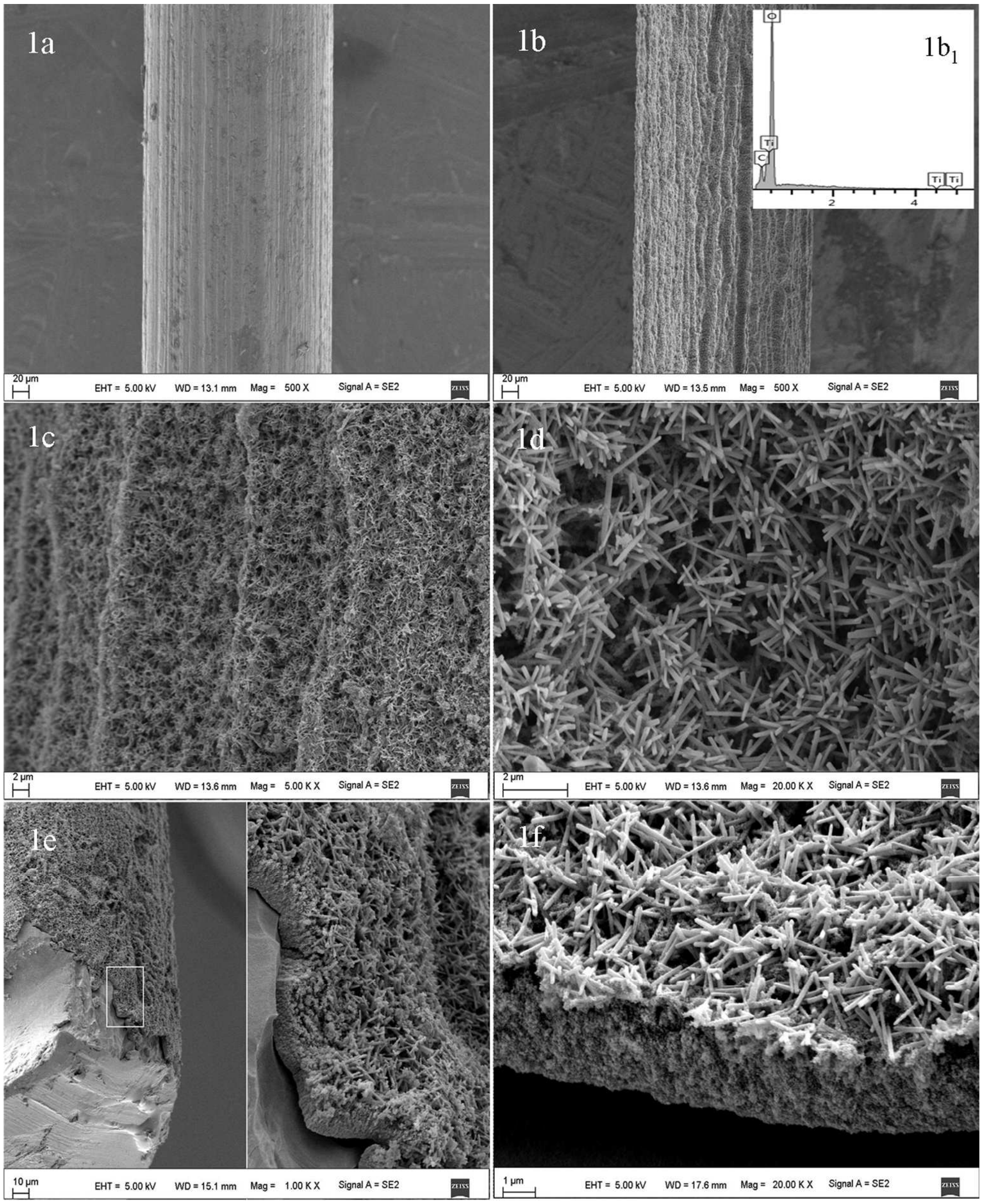

Figure 1. SEM images of bare Ti wire (a) and rod-like TiO2 coated fiber. (b), (c) and (d) the top view; (e) the cross section view; (f) the side view.
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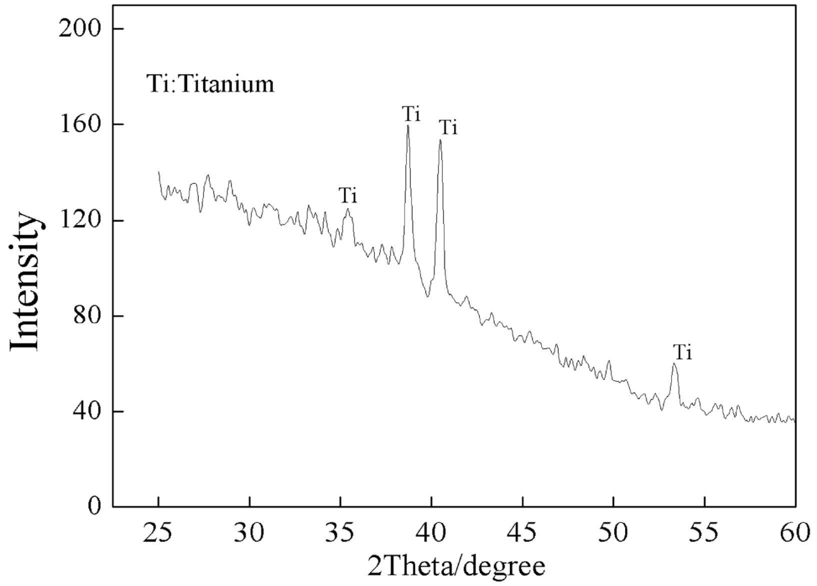

Figure 2. X-ray diffraction patterns of rod-like TiO2 coating by anodic oxidation.
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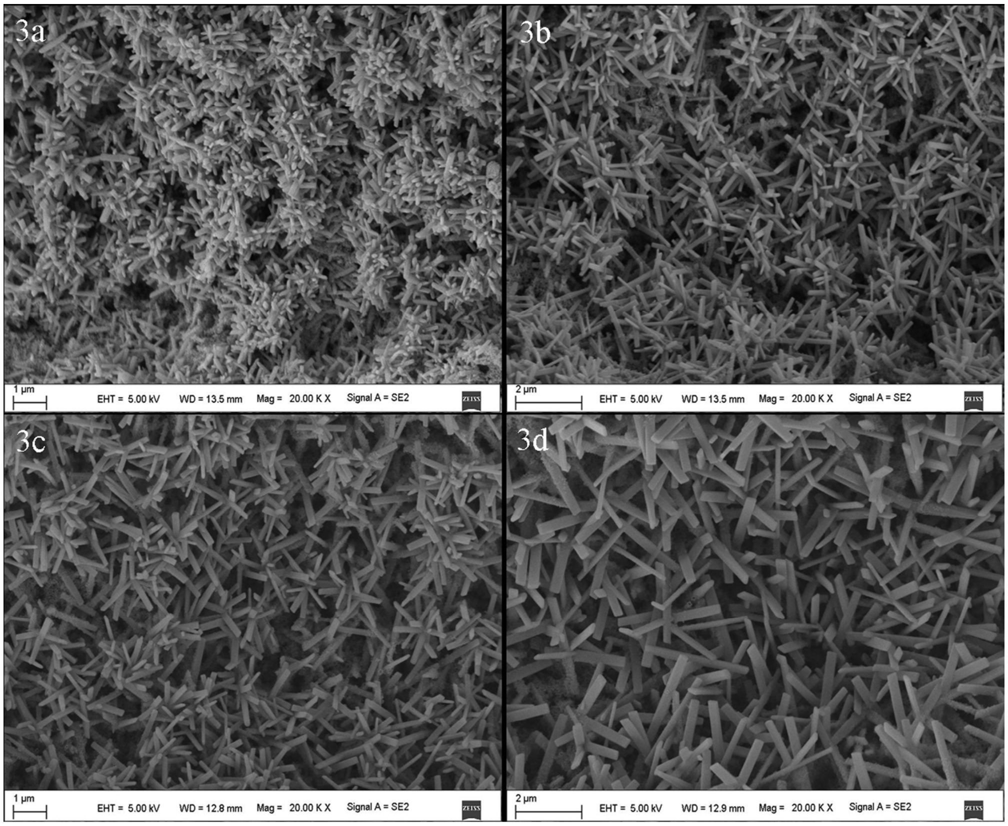

Figure 3. SEM images of the as-fabricated fibers by anodization within 30 min (a), 45 min (b), 60 min (c) and 90 min (d).
180x147mm (300 x 300 DPI)

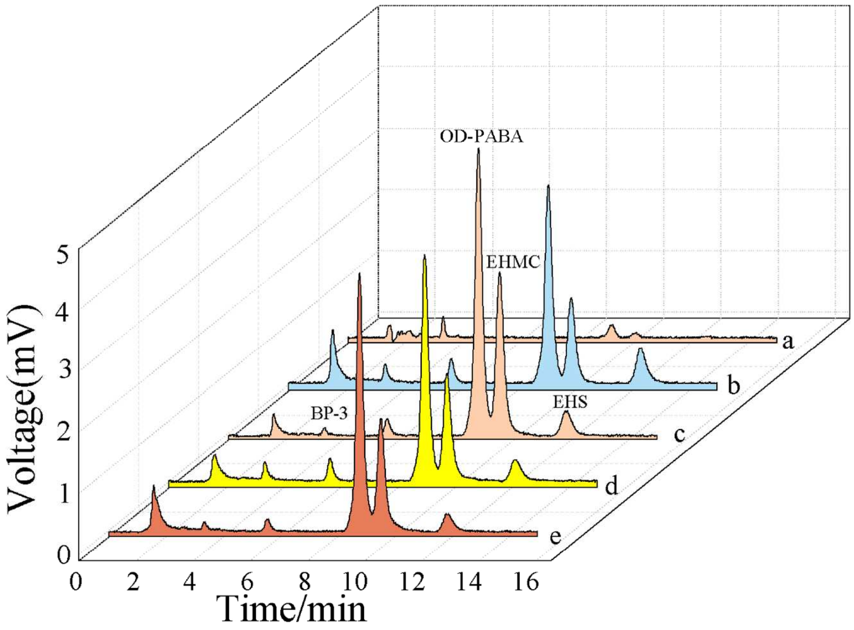

Figure 4. Chromatograms of direct HPLC (a) and SPME-HPLC with the as-fabricated fibers by anodization in 30 min (b), 45 min (c), 60 min (d) and 90 min (e).
209x148mm (300 x 300 DPI)

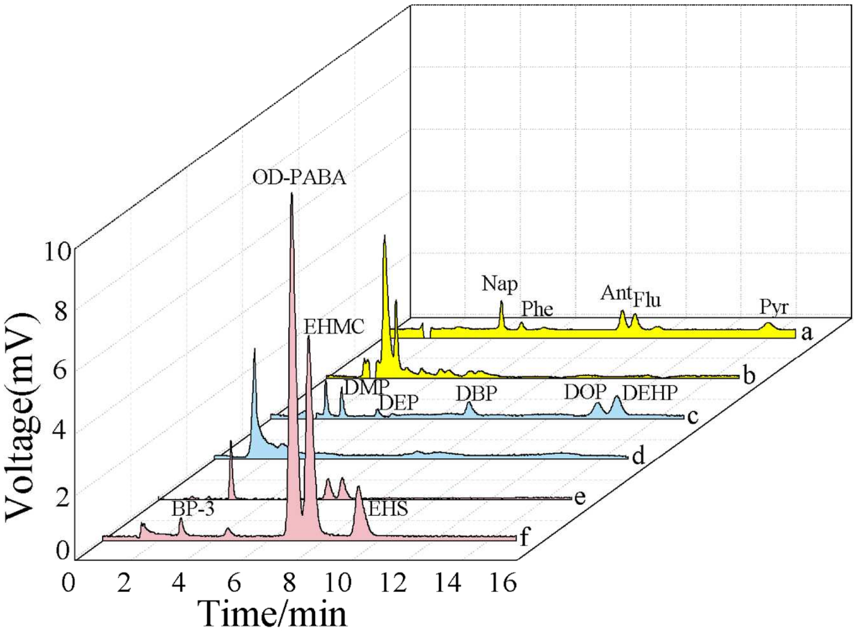

Figure 5. Typical chromatograms of direct HPLC for PAHs (a), PAEs (c) and UV filters (e) spiked water with 100 µg•L-1 as well as corresponding SPME-HPLC with the rod-like TiO2 coated fiber for PAHs (b), PAEs (d) and UV filters (f).
209x148mm (300 x 300 DPI)

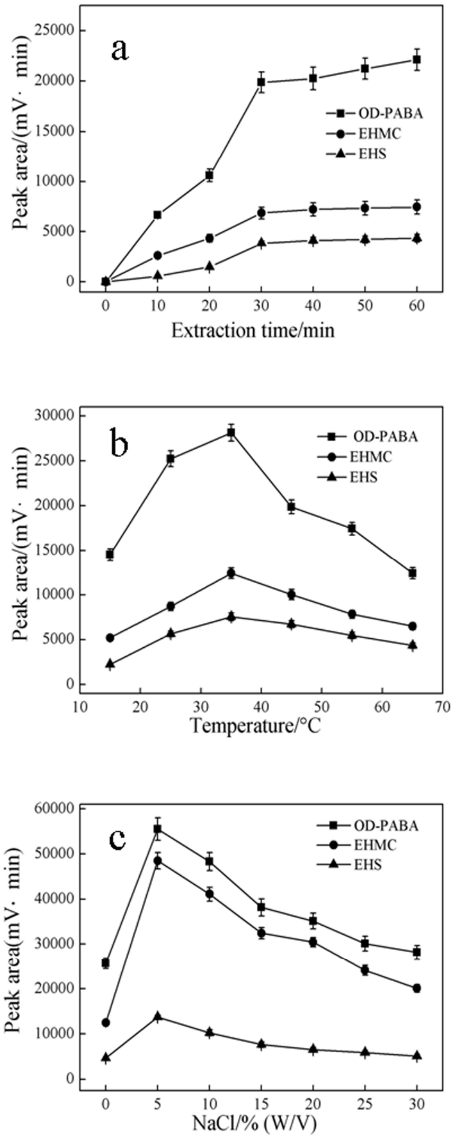

Figure 6. Effect of extraction time, temperature, NaCl on the extraction efficiency.
281x633mm (300 x 300 DPI)

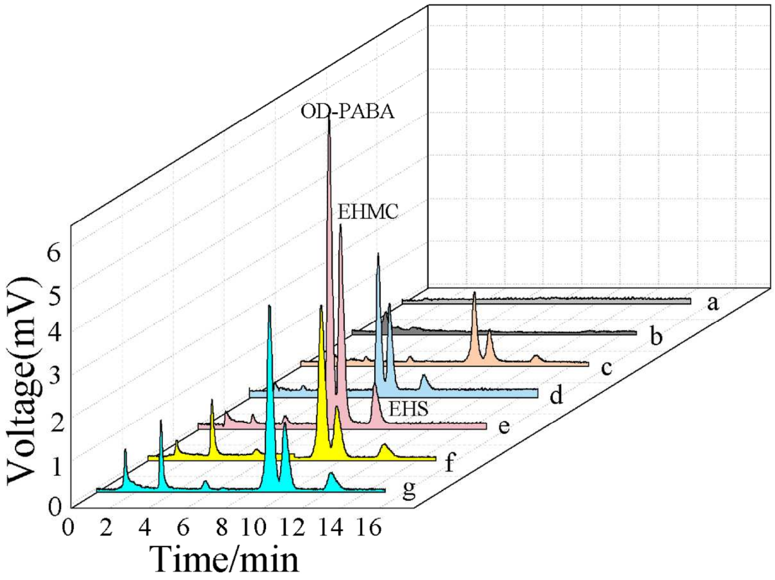

Figure 7. Chromatograms of direct HPLC and SPME-HPLC for real and spiked river water under Bapanxia Bridge. Direct HPLC (a) and SPME-HPLC with the rod-like TiO2 coated fiber (b) for real river water; SPME-HPLC with the rod-like TiO2 coated fiber for spiked river water at 5 µg•L-1 (c), 25µg•L-1 (d) and 50 µg•L-1 (e); SPME-HPLC with 100 µm PDMS (f) and 85 µm PA fibers (g) for spiked river water at 50 µg•L-1.
209x148mm (300 x 300 DPI)

Table 1

Analytical parameters of the proposed method (n=5)

UV filters	Linear range ($\mu g\cdot L^{-1}$)	r^2	Recovery (%)	Single fiber repeatability Intraday (%)	Single fiber repeatability Interday (%)	Fiber-to-fiber reproducibility (%)	LOD ($\mu g\cdot L^{-1}$)
OD-PABA	0.05 -200	0.9980	90.68	5.44	5.71	8.63	0.024
EHMC	0.05-200	0.9972	92.72	6.68	7.13	7.41	0.023
EHS	0.1-200	0.9976	102.6	7.21	7.81	8.26	0.032

Table 2

Analytical results of UV filters in different environmental water samples (n=3)

Samples	UV filters	Original ($\mu g\cdot L^{-1}$)	Spiked with 5 $\mu g\cdot L^{-1}$			Spiked with 25 $\mu g\cdot L^{-1}$			Spiked with 50 $\mu g\cdot L^{-1}$		
			Detected ($\mu g\cdot L^{-1}$)	Recovery (%)	RSD (%)	Detected ($\mu g\cdot L^{-1}$)	Recovery (%)	RSD (%)	Detected ($\mu g\cdot L^{-1}$)	Recovery (%)	RSD (%)
River water under Bapanxia Bridge	OD-PABA	ND [a]	4.62	92.40	6.41	21.84	87.36	7.62	42.34	84.68	8.10
	EHMC	ND [a]	4.84	96.8	7.43	23.31	93.24	6.82	46.54	93.08	8.82
	EHS	ND [a]	5.24	104.8	8.94	23.42	93.68	8.31	43.12	86.24	7.37
River water under Donggang Bridge	OD-PABA	5.12	9.12	90.12	8.43	28.23	93.73	9.82	53.56	97.16	9.43
	EHMC	4.67	9.86	101.9	9.46	28.04	94.50	8.23	54.11	98.97	9.14
	EHS	4.54	9.75	102.2	8.26	27.12	91.80	9.34	52.14	95.60	7.87
River water under Shichuan Bridge	OD-PABA	3.12	8.43	103.8	7.18	26.92	95.73	8.17	49.84	93.82	8.56
	EHMC	4.86	8.89	90.16	6.94	27.61	95.67	7.42	53.21	96.99	9.51
	EHS	4.81	8.92	90.93	6.64	30.12	101.4	9.12	49.92	91.08	7.43

Influent from wastewater treatment plant	OD-PABA	6.72	11.92	101.7	8.48	30.85	97.25	8.65	52.31	92.22	7.41
	EHMC	5.42	9.46	90.78	8.72	28.42	93.42	9.38	51.78	93.43	8.85
	EHS	4.48	8.82	93.04	9.71	27.03	91.69	9.67	50.26	92.25	9.74

a) ND, Not detected or lower than LOD.