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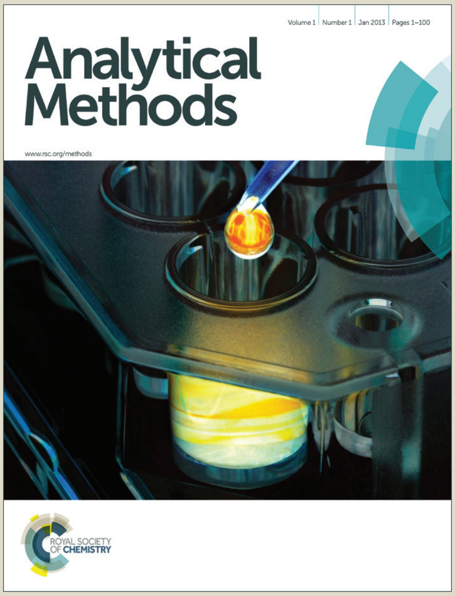

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Rapid electrochemical preparation of porous sponge-like zinc-zinc oxide coating deposited on an etched stainless steel fiber for selective determination of UV filters in environmental water samples

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Abstract: A novel porous sponge-like zinc-zinc oxide (Zn-ZnO) coating was directly prepared on an etched stainless steel wire substrate as solid-phase microextraction (SPME) fiber via previous electrodeposition of robust ZnO coating. The scanning electron micrograph of the Zn-ZnO coated fiber exhibits a porous spongy nanostructure with high surface area. The SPME performance of the prepared 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 porous sponge-like Zn-ZnO coating exhibited high extraction capability, good selectivity and rapid mass transfer for some UV filters. The main parameters affecting

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extraction performance were investigated and optimized. Under the optimized conditions, the calibration graphs were linear over the range of 0.1-200 $\mu g\cdot L^{-1}$. The limits of detection of the proposed method were 0.032-0.064 $\mu g\cdot L^{-1}$ (S/N=3). The single fiber repeatability varied from 5.5% to 7.2% and the fiber-to-fiber reproducibility ranged from 7.1% to 8.3% for the extraction of spiked water with 50 $\mu g\cdot L^{-1}$ UV filters (n=5). The established SPME-HPLC-UV method was successfully applied to the selective concentration and sensitive determination of target UV filters from real environmental water samples with recoveries from 80.3% to 99.2% at the spiking level of 5 $\mu g\cdot L^{-1}$ and 50 $\mu g\cdot L^{-1}$. The relative standard deviations were below 9. 3%.

Keywords: Porous sponge-like Zinc oxide； Stainless steel fiber; Electrodeposition; Ultraviolet filters; Solid-phase microextraction

1. Introduction

Solid-phase microextraction (SPME) is an environmentally friendly and attractive solvent-free sample preparation technique which integrates sampling,extraction, preconcentration and sam-ple introduction in a single step [1]. It integrates sample extraction, concentration and introduction into one step, and easily coupled to gas chromatography (GC) and high-performance liquid chromatography (HPLC). As compared with traditional liquid-liquid extraction and solid-phase extraction, SPME is a simple, time-saving, sensitive and solvent-free technique by integrating sampling, extraction, concentration with sample introduction procedures for gas chromatography and high performance liquid chromatography (HPLC) in a single step [2]. This technique is subjected to the partitioning of the organic analytes between the sample matrix and thin extraction coating deposited onto a fused silica fiber. 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 solvent, 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. Currently, commercially available fibers have polymeric coatings such as polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene, carboxen, carbowax and their composites[3]. However, most of them are expensive and also suffer from fragility, low thermal and chemical stability, stripping of coatings and easily swelling in organic solvents, which limit their widespread applications. Recently more attention has been paid to the use of synthesized nanomaterials as extraction coatings in the preparation of SPME fibers [4]. These nanostructured coatings involve unique surface structures and properties which improves the extraction efficiency, selectivity and mass transfer of specific analytes. In particular, strong adhesion of uniform nanomaterial coatings onto metallic supports greatly improves the flexibility of the fibers and significantly prolongs the lifetime of the fibers. For these reasons, many efforts have been devoted to the development of special nanomaterials coated metal-based supports such as stainless steel (SS) wires [5-9], silver wire [10], platinum wires [11-13] and titanium wires [14-18]. Due to their quite different physicochemical properties from fused-silica fiber, there have been a variety of preparation strategies for nanomaterial coatings with the metal wires as supporting substrates. These metal wire supported fibers are physically strong and can be handled with great convenience.

SS wire is inexpensive and frequently used as supporting substrates in preparing novel SPME fibers [5-9,19,20]. For the purpose of tight attachment of coating materials to the SS substrates, however, the SS wire often needed some additional pretreatments before subsequent coating procedure [21,22]. Chemical etching is very promising for increasing the surface area of SS wire [23]. The etched SS wire seems to be a promising alternative substrate for further fabrication and strong adhesion of highly efficient coating materials to the SS substrate because it exhibits much larger surface area and more active sites [24-26]. Electrochemical deposition allows to precisely control coating uniformity, thickness and deposition rate for conductive coatings. This technique is especially attractive for further deposition onto the substrates with complex shapes [27].

Zinc oxide (ZnO) is a promising material due to its good thermal stability, no toxicity, biocompatibility and easy preparation [28]. The as-prepared one-demensional ZnO coatings proved to exhibit satisfactory extraction capability for the selected organic compounds due to their high surface-to-volume ratio. The first report about the application of ZnO-coated SPME fiber was presented for the extraction of thiophenol from water samples by Djozan and co-workers [29]. The results showed that the proposed fiber was selective for polar compounds. In recent years, ZnO nanorods and nanotubes have been prepared on fused silica fibers as SPME coatings based on hydrothermal synthesis method [30-33]. However, the SPME fibers based on the fused silica support are easily broken and therefore their service life is limited. For this reason, ZnO nanorods coated SS wires were prepared using in situ hydrothermal growth method [34,35]. The prepared fibers showed excellent extraction efficiency for benzene homologues and aldehydes. Furthermore, developing simple, rapid and low-cost preparation strategies to fabricate ZnO nanostructures for SPME coatings is also desirable. Thus, it is interesting and innovative work to fabricate a ZnO-based coating with alternative nanostructure and to find its potential applications in water analysis. In the present work, we presented a new approach to rapid and uniform electrodeposition of robust Zn coating on the surface of the etched SS wire using potentiostatic technique followed by its spontaneous oxidation in air. This proposed procedure is simpler and more convenient than hydrothermal synthesis method. Extraction capability and selectivity of the Zn-ZnO coated fiber were investigated for the concentration and determination of trace polycyclic aromatic hydrocarbons (PAHs), phthalates (PAEs) and ultraviolet (UV) filters coupled to HPLC with UV detection (HPLC-UV). Finally, this novel fiber was practically applied to the selective concentration and sensitive determination of trace target UV filters from different environmental water samples. Its SPME performance was also compared with that of commercial PDMS and PA fibers under the optimized conditions.

2. Experimental

2.1. Materials and reagents

Stainless steel wire (0.20 mm O.D.) was obtained from Gaoge (Shanghai, China). A polyacrylate (PA, 85 μm thickness) and polydimethylsiloxane (PDMS, 100 μm thickness) fibers were obtained from Supelco (Bellefonte, PA, USA). 0.45 μm micropore membrane of polyvinylidene fluoride was supplied by Xingya Purifying Material Factory (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). Hydrouoric acid (HF) was obtained from Yantai Shuangshuang Chemicals Ltd (Shandong, China). 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-(*N,N*-dimethylamino) benzoate (OD-PABA) and 2-ethylhexyl 4-methoxycinnamate (EHMC) were purchased from AccuStandard (New Haven, CT, USA). Certified individual standards of naphthalene (Nap), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu) and pyrene (Pyr) were purchased from Aldrich (St. Louis, MO, USA). Certified 2-ethylhexyl salicylate (EHS) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). Stock standard solutions of 100 mg·L^{-1} each compound were 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. Apparatus

Chromatographic separation was 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 chromatographic workstation (Zhejiang University, China). Sample stirring and heating was carried out in a DF-101S water bath with magnetic stirrer and a temperature-controlled system (Changcheng, Zhengzhou, 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). Electrodeposition of Zn coating was performed on a CHI832D electrochemical analyzer (Shanghai, China). The morphologies of the prepared fiber were investigated by an Ultra Plus microscope (Zeiss, Oberkochen, Germany) with an energy dispersive X-ray spectrometer (EDS).

2.3. Preparation of Zn-ZnO coated fiber

A piece of SS wire (75 mm×0.20 mm O.D.) was washed with methanol, acetone and ultrapure water in an ultrasonic bath. Thereafter 2-cm segment of the SS wire was dipped into in hydrofluoric acid of 40% for chemical etching for 60 min at 40 °C. After the etched SS wire was thoroughly washed with methanol and ultrapure water in an ultrasonic bath, the etched segment was immersed into the electrolytic solution with different amounts of $Zn(NO_3)_2$ and 0.05mol/L Hexamethylenetetramine(HMT) [34]. Electrodeposition of Zn coating was performed at applied potential of -1.4V at 25±1 °C in a three-electrode configuration with the platinum rod as a counter electrode, the saturated calomel electrode as a reference electrode and the etched SS wire as a working electrode. Subsequently the Zn coating electrodeposited on the etched SS wire was rinsed with ultrapure water and allowed spontaneous oxidation for the formation of compact and stable ZnO coating on the surface of the active Zn coated fiber in the atmosphere.

2.4. Sample collection

Real environmental water samples include 4 river water (pH, ~7.5) and 1 wastewater samples (pH, ~7.93). River water samples were collected at different sites of Lanzhou section of the Yellow River. A wastewater sample was collected from a local wastewater treatment plant. All real water samples were freshly collected in amber glass containers and filtered through 0.45 μm micropore membranes, stored in the refrigerator at 4 ^{o}C.

2.5. SPME-HPLC procedure

The extraction was carried out with 15 mL of working standard solution or sample solution in a 20 mL glass vial with a magnetic stir bar. The prepared fiber was directly immersed into the sample solution for a period of time at elevated temperature. After extraction, the fiber was retracted from the sample solution and immediately 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. The mobile phase consists of methanol and water of 90/10 (v/v), 70/30 (v/v) and 85/15 (v/v) at a flow rate of 1 mL·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 porous sponge-like Zn-ZnO coated fiber

Acid etching was performed to increase surface roughness of the SS wire and improve the attachment of Zn coating onto the surface of SS wire. The etched SS wire shows very rough surface structure and thereby offers very large contact surface. Fig. 1 illustrates scanning electron microscopy (SEM) images of the SS wires before (Fig. 1a) and after chemical etching (Fig. 1b). When the etched SS wire was used as a cathodic electrode in the presence of $Zn(NO_3)_2$, a porous sponge-like coating was formed on the etched SS wire after electrodeposition (Fig. 1c and 1d). We had measured the pore property of new materials it shows about 600 nm. This unique nanostructure was interconnected and tightly attached onto the etched SS wire substrate. Indeed it possesses much larger surface area, more open access sites and better durability, which are most desirable for efficient SPME.

The surface composition of the porous sponge-like coating was studied by EDS. The spectrum obtained for the etched SS surface exclusively shows some peaks corresponding to the presence of Cr, Fe and Ni (Fig. 2a) which are components of original SS wire. After electrodeposition, strong peaks of zinc and oxygen also appear at 1.0 keV and 0.5 keV (Fig. 2b), respectively. This result clearly indicates that Zn coating was successfully electrodeposited on the etched SS substrate and full coverage on the etched SS substrate was achieved. Spontaneous oxidization of active Zn coating electrodeposited on the etched SS wire should be responsible for the formation of the porous sponge-like ZnO coating.

Fig. 1.

Fig. 2.

3.2. Optimization for preparation of porous sponge-like Zn-ZnO coated fiber

The extraction performance of solid coating materials greatly depends on their structure and surface properties. For this purpose, dependence of Zn-ZnO coating on $Zn(NO_3)_2$ concentration and electrodeposition time was further investigated and optimized. Fig. 3 exhibits SEM images of some prepared fibers at different concentrations of $Zn(NO_3)_2$. In the presence of 0.05 $mol{\cdot}L^{-1}$ $Zn(NO_3)_2$, uniform and robust ZnO coating was obtained. Moreover, as shown in Fig. 4, the compact and uniform Zn-ZnO coating with a porous sponge-like nanostructure was observed for the electrodeposition of Zn within 10 min. Therefore the electrochemical deposition of porous sponge-like Zn-ZnO coating was performed in the solution of 0.05 $mol{\cdot}L^{-1}$ $Zn(NO_3)_2$ for 10 min in the electrochemical procedure.

Fig. 3.

Fig. 4.

3.3. Extraction selectivity of porous sponge-like Zn-ZnO coated fiber

The extraction selectivity of the porous sponge-like Zn-ZnO coated fiber was further studied for SPME of PAEs (DMP, DEP, DBP, DOP and DEHP), PAHs (Nap, Phe, Ant, Flu and Pyr), and UV filters (BP-3, OD-PABA, EHMC and EHS) from aqueous phase. As shown in Fig. 5, this fiber exhibits excellent extraction selectivity for BP-3, OD-PABA and EHMC while no extraction capability toward PAEs, PAHs and EHS occurs. This result may be attributed to the inherent physicochemical nature of sponge-like ZnO coatings. On the one hand, the sponge-like ZnO exhibit strong affinity for polar organic compounds due to the presence of Zn-OH at the surface of ZnO coating. On the other hand, it is expected that strong Lewis acidic sites at the surface of sponge-like ZnO would show good affinity for BP-3, OD-PABA and EHMC (with Lewis basic property). Such a ZnO nanostructure provides a potential approach to selective extraction of BP-3, OD-PABA and EHMC from complex environment water samples and greatly enhances their extraction efficiency due to its high surface-to-volume ratio.

Fig. 5.

3.4. Optimization of SPME conditions

In order to optimize the extraction behavior of the porous sponge-like Zn-ZnO coating towards UV filters, the experimental variables affecting the extraction efficiency including temperature, extraction and desorption time, stirring rate and salt addition were investigated with working solution at spiking level of 20 $\mu g \cdot L^{-1}$ each analyte.

3.4.1. Effect of extraction and desorption time

Extraction time is a crucial factor in SPME. Fig. 6a shows the extraction time profile of BP-3, OD-PABA and EHMC. Three UV filters reached extraction equilibrium after exposure of the Zn-ZnO coated fiber to the stirred solution for 40 min. The equilibration time clearly indicates that the porous sponge-like Zn-ZnO coating allows for rapid mass transfer from bulk solution to the fiber. Meanwhile constant desorption maximum was achieved for target UV filters within 3 min in the case of static solvent desorption in mobile phase. Thus extraction of 40 min and desorption of 3 min were employed in the following studies.

Fig. 6.

3.4.2. Effect of extraction temperature

Temperature is very important for SPME because of its potential influence on the mass transfer and the partitioning of target analytes between fiber coating and sample solution.

The effect of temperature on the extraction was investigated from 35 to 60 □. As shown in Fig. 6b, the extraction efficiency increased up to 50□. Subsequently, the extraction capability decreased at higher temperature. This result can be ascribed to their decreased distribution coefficients between the Zn-ZnO coating and aqueous phase because adsorption is generally an exothermic process [35]. In addition, the increased solubility of target UV filters also results in decreased extraction efficiency at higher temperature. Therefore, 50□ was selected as the optimal extraction temperature in this study.

3.4.3. Effect of stirring rate

Stirring improves the extraction efficiency through accelerating mass transfer of the analyte molecules from sample solution to the fiber coating. As shown in Fig. 6c, the extraction efficiency maximum of BP-3, OD-PABA and EHMC was achieved at the stirring rate of 300 $r \cdot min^{-1}$. Thereafter, more vigorously stirring might lead to tiny bubble formation which is unfavorable to the adsorption of analyte molecules onto the surface of the porous sponge-like Zn-ZnO coating. Therefore, 300 $r \cdot min^{-1}$ was used in following experiments.

3.4.4. Effect of salt

Addition of salt usually decreases the solubility of organic analytes in aqueous phase due to the formation of hydration spheres around the ionic salt molecules, which increases their concentrations in fiber coating. This effect leads to varying the partition coefficient of analytes between fiber coating and sample solution, and thereby the extraction efficiency may be changed. Thus effect of salt was examined by addition of NaCl into the working solutions.

As shown in Fig. 6d, a positive effect on extraction of BP-3, OD-PABA and EHMC was observed in aqueous phase with NaCl of 5% (w/v). At higher concentration, more salt addition also leads to an increase in sample viscosity and results in a negative effect on their extraction.In this case, the salting-out effect plays a major role. Therefore, NaCl of 5% (w/v) was used in subsequent studies.

3.5. Analytical performance

The analytical performance of the porous sponge-like Zn-ZnO 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 Zn-ZnO coated fiber exhibited wide linearity with 3 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 5.45% to 7.03% and from 6.02% to 7.36% for intraday and interday SPME-HPLC of UV filters, respectively. The fiber-to-fiber reproducibility for five parallel prepared fibers ranged from 7.12 % to 8.33%.

3.6. Analysis of real samples

UV filters are substances that are able to filter UV radiation and thus protect human skin from direct exposure to the deleterious wavelengths of sunlight [36]. Their detection has clearly demonstrated that UV filters are directly or indirectly discharged into aquatic environment during bathing and washing activities via domestic wastewater [37]. A preliminary study reported that some UV filters are estrogenic, antiestrogenic, androgenic and antiandrogenic in vitro and in vivo [38]. With the increasing use of UV filters in daily care products, the environmental impact of UV filters has aroused great concern. Therefore real water samples were collected from local river and urban wastewater treatment plant. The proposed method was applied to the selective preconcentration and determination of target UV filters in real water samples. The results of three replicate analyses were listed in Table 2 for real environmental water spiked with UV filters of 5 $\mu g \cdot L^{-1}$ and 50 $\mu g \cdot L^{-1}$. Fig. 7 shows typical chromatograms obtained for SPME-HPLC of target UV filters in raw influent with the Zn-ZnO coated fiber. The matrix effect was minor. As compared with commercially available 100-μm PDMS (Fig. 7e) and 85-μm PA fibers (Fig. 7f), the Zn-ZnO coated fiber (Fig. 7d) exhibits the best extraction efficiencies for target UV filters. These results clearly demonstrate that the novel Zn-ZnO porous spongy coated fiber is reliable and suitable for selective preconcentration and sensitive determination of trace target UV filters in environmental water samples.

Fig. 7.

3.7. Stability and durability

The stability of the porous sponge-like Zn-ZnO coating was examined after exposure to methanol, tetrahydrofuran, dimethylsulfoxide and chloroform for 48 h, respectively. It has been found that the Zn-ZnO coated fiber is stable and can not suffer from any damage in these organic solvents based on its SEM images. In the experiment, the Zn-ZnO coated fiber has withstood at least 150 times successive extraction and desorption runs in mobile phase according to the prescribed experimental procedures. The recovery from 96.3%-102% was also obtained for five replicate analyses of spiking water with 50 $\mu g \cdot L^{-1}$. Furthermore, this fiber is still reusable after a month storage, indicating that the porous sponge-like Zn-ZnO composite coating was tightly attached to the etched SS wire substrate. Its mechanical and chemical stability clearly demonstrate that the porous sponge-like Zn-ZnO coated fiber will find its practical applications in environmental water analysis in the future.

3.8. Comparison of the proposed method with reported methods

Some statistical data are presented in Table 3 with respect to extraction time (t), linear ranges, RSD, LOD and recovery. It can be seen that extraction time and LOD values of the proposed method with porous sponge-like Zn-ZnO coated fiber were comparable or better than those reported in the literatures [16,37,40-43]. This might be due to the fact that the Zn-ZnO composite coating possesses porous sponge-like nanostructure and increases available surface area. This unique nanostructure will be able to enhance adsorption efficiency for target analytes. Furthermore, the preparation of the porous sponge-like Zn-ZnO coating is simple, rapid and reproducible.

4. Conclusions

In this study, a novel porous sponge-like Zn-ZnO coated fiber was directly fabricated onto an etched SS substrate by electrodeposition of Zn coating in a highly reproducible manner and its SPME performance was evaluated by different kinds of analytes in detail. Due to its unique porous sponge-like nanostructure, the Zn-ZnO composite coating has high surface-to-volume ratio and open access sites for adsorption of target analytes and exhibits high extraction capability, good selectivity and fast mass transfer for SPME of BP-3, OD-PABA and EHMC. Furthermore the developed fiber is more effective than the commercially available PDMS and PA fibers for SPME of target UV filters. In addition, the porous sponge-like Zn-ZnO composite coating was tightly attached onto the rough surface of the etched SS wire substrate via the electrodeposition of robust Zn coating. The developed SPME-HPLC-UV method provided a simple, fast, and precise approach for selective concentration and sensitive determination of target UV filters from environmental water samples. Furthermore this controllable Zn-ZnO coating deposited on an etched SS substrate can serve as a nanoporous support for subsequent fabrication and surface modification in the future.

Acknowledgements

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Figure captions

Fig. 1. SEM micrographs of untreated SS wire (a×1000) and etched SS wire (b×1000) and Zn-ZnO coating (c×1000 and d×50000).

Fig. 2. EDS of the etched SS wire (a) and the porous sponge-like Zn-ZnO coating (b).

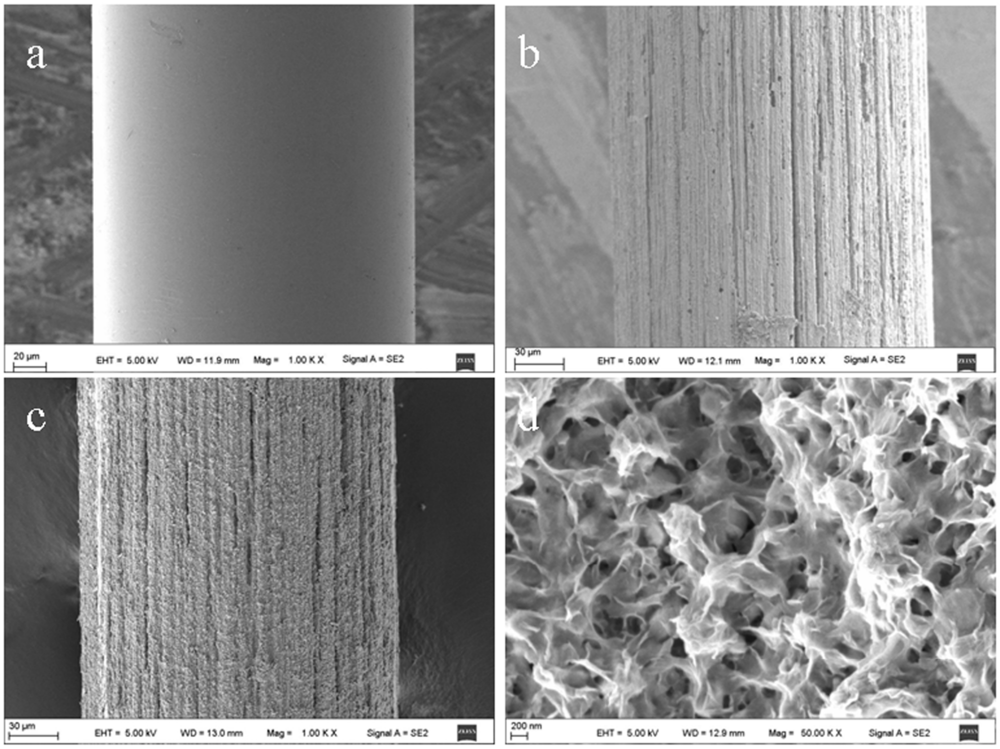
Fig. 3. SEM micrographs of the Zn-ZnO coating prepared in $Zn(NO_3)_2$ solution of 0.025 $mol \cdot L^{-1}$ (a), 0.05 $mol \cdot L^{-1}$ (b), 0.075 $mol \cdot L^{-1}$ (c) and 0.1 $mol \cdot L^{-1}$ (d).

Fig. 4. SEM micrographs of the porous sponge-like Zn-ZnO coating prepared within 5 min (a), 10 min (b), 15 min (c) and 20 min (d).

Fig. 5. Typical chromatograms of direct HPLC for PAHs (a), PAEs (c) and UV filters (e) as well as corresponding SPME-HPLC with Zn-ZnO coated fiber for PAHs (b), PAEs (d) and UV filters (f) at spiking level of 50 $\mu g \cdot L^{-1}$ each analyte.

Fig. 6. Effect of extraction time (a), temperature (b), stirring rate (c) and ionic strength (d) on extraction efficiency.

Fig. 7. Chromatograms of direct HPLC and SPME-HPLC for raw and spiking influents. Direct HPLC for raw influent (a); SPME-HPLC with Zn-ZnO coated fiber for raw influent (b), spiking influent at 10 $\mu g \cdot L^{-1}$ (c) and spiking influent at 50 $\mu g \cdot L^{-1}$ (d); SPME-HPLC with 100-μm PDMS (e) and 85-μm PA fibers (f) for spiking influent at 50 $\mu g \cdot L^{-1}$.



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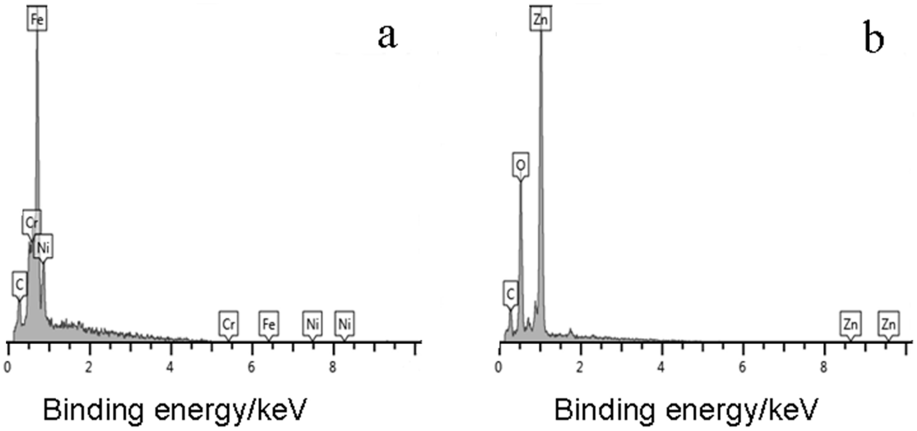

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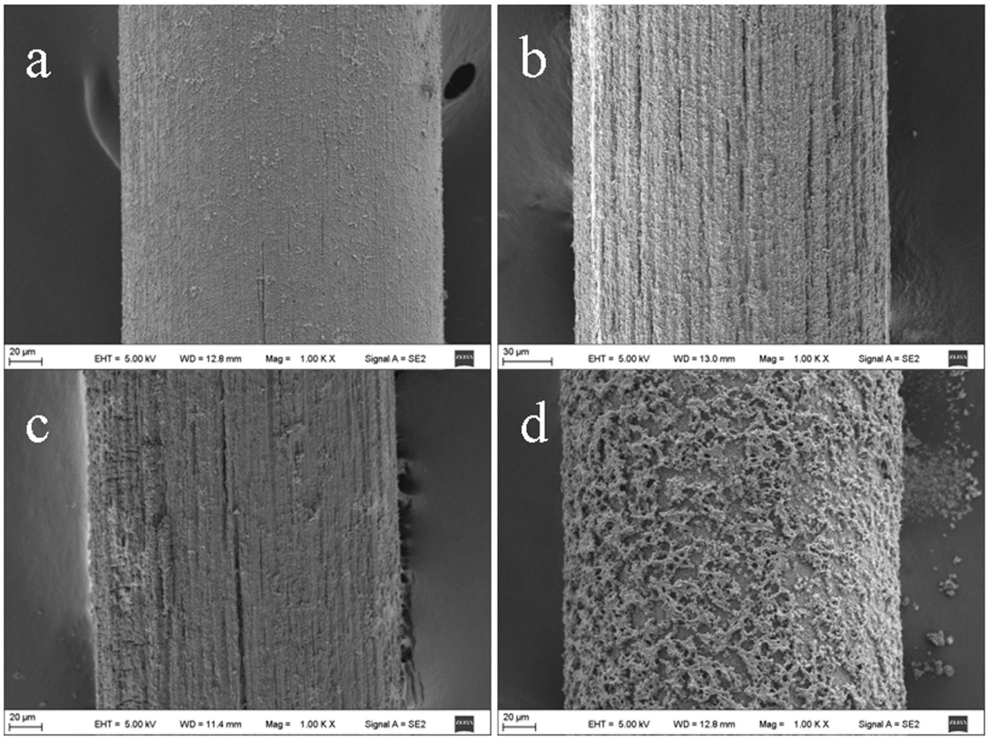

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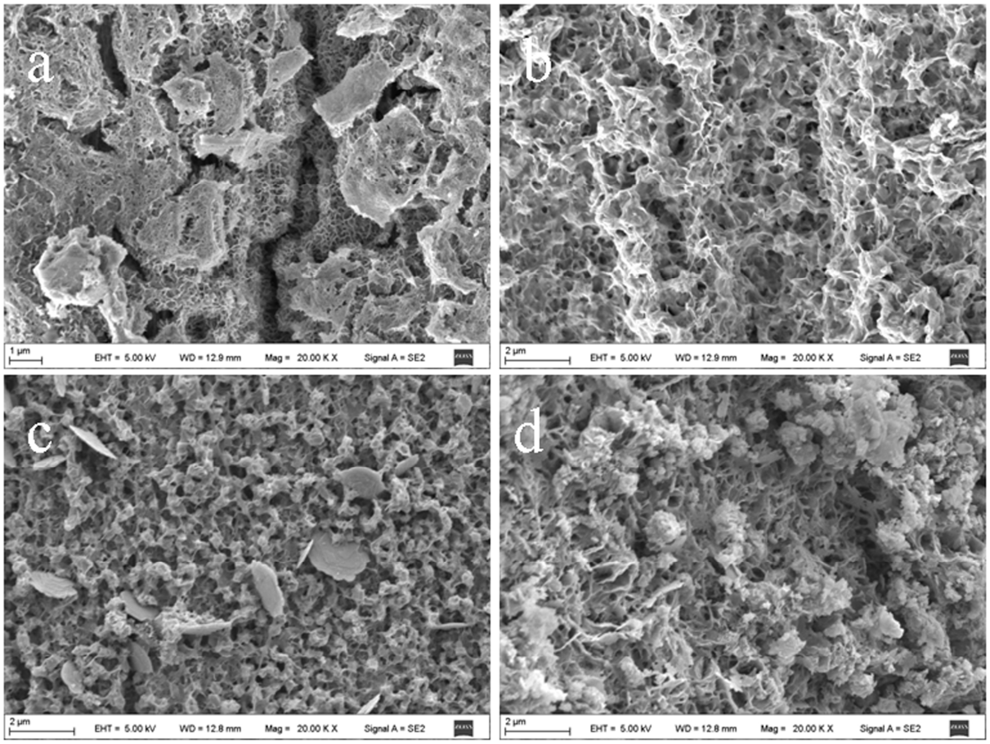

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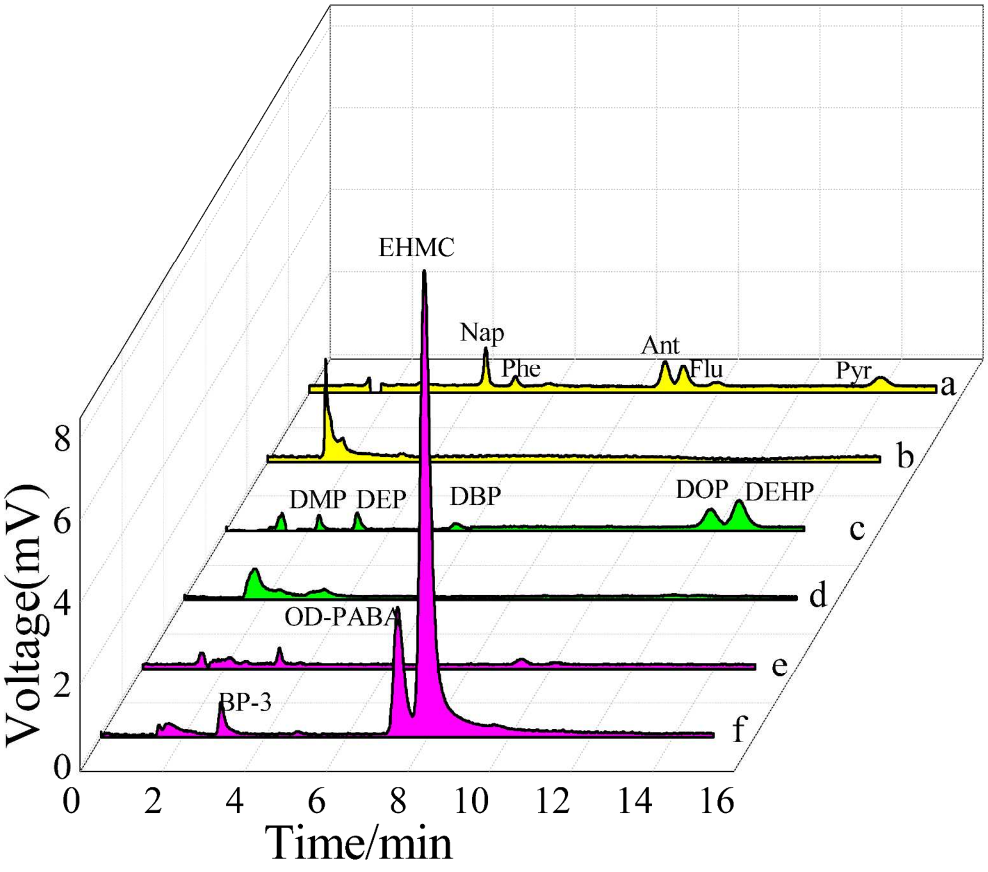

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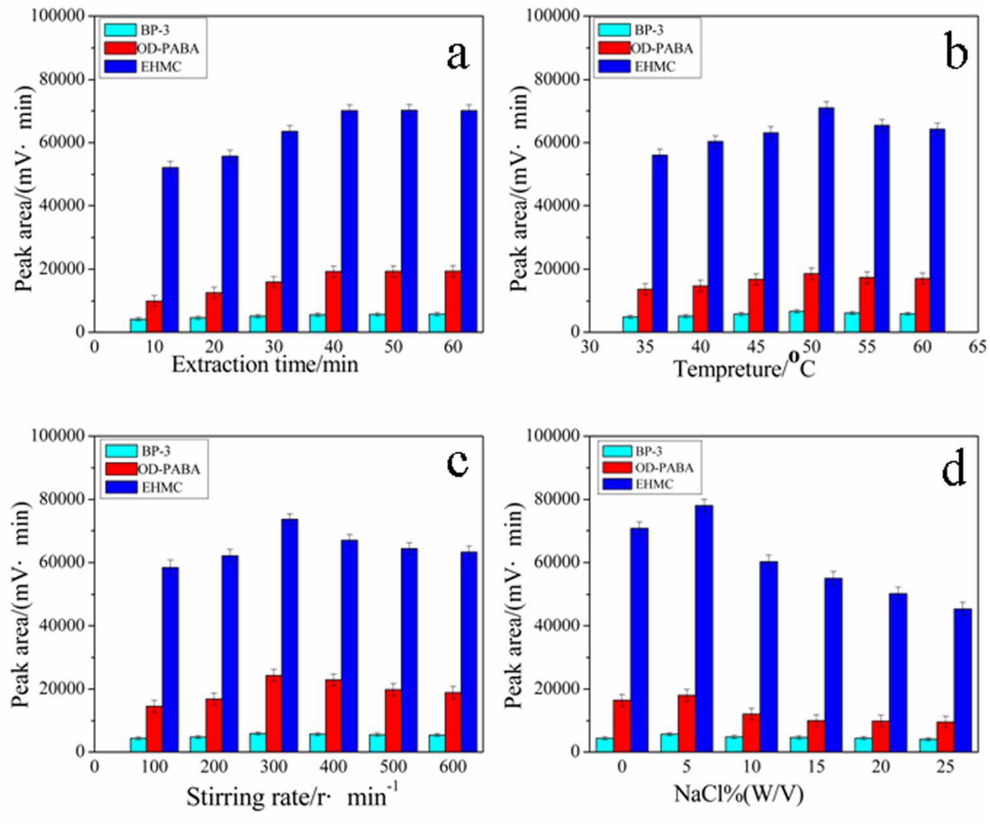

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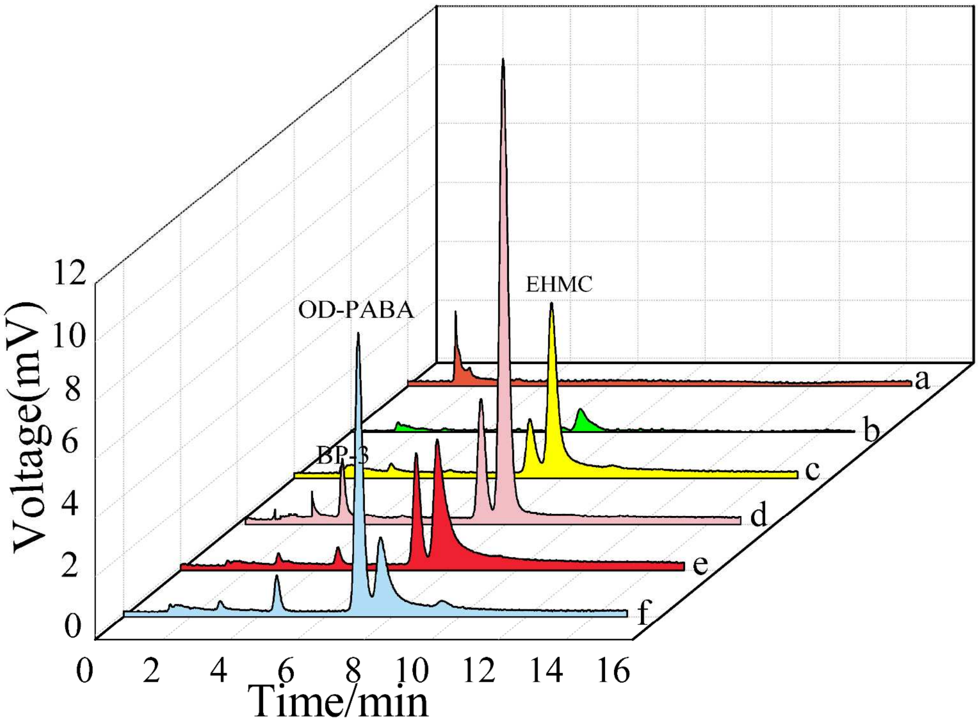

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Table 1

Analytical parameters of the proposed method (n=5)

UV filters	Linear ranges (μg·L^{-1})	r^2	Recovery (%)	Single fiber repeatability		Fiber-to-fiber reproducibility (%)	LOD (μg·L^{-1})
				Intraday (%)	Interday (%)		
BP-3	0.1-200	0.9992	96.3	7.0	7.4	8.0	0.064
OD-PABA	0.1-200	0.9995	99.5	6.9	7.2	8.3	0.032
EHMC	0.1-200	0.9997	102	5.5	6.0	7.1	0.053

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 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	BP-3	ND [a]	4.58	91.6	6.7	46.4	92.8	6.7
	OD-PABA	ND	4.21	84.2	6.8	47.2	94.4	5.5
	EHMC	ND	4.96	99.2	7.2	48.1	96.2	9.3
River water under Yintan Bridge	BP-3	ND	4.32	86.4	8.3	49.3	98.6	7.4
	OD-PABA	3.22	7.01	85.3	7.1	51.5	96.8	8.2
	EHMC	4.28	8.03	86.5	6.9	53.3	98.2	9.5
River water under Donggang Bridge	BP-3	2.21	6.90	95.7	6.3	51.9	99.4	8.5
	OD-PABA	4.83	9.08	92.4	7.2	53.3	97.2	8.0
	EHMC	5.82	9.32	94.9	8.7	54.6	97.8	8.5
River water under Shichuan Bridge	BP-3	2.17	6.48	90.4	6.7	51.8	99.3	9.3
	OD-PABA	2.58	6.09	80.3	8.6	50.1	95.3	8.8
	EHMC	3.26	7.68	93.0	8.1	52.8	99.1	7.5

Influent wastewater	BP-3	5.59	10.5	99.2	7.6	53.7	96.6	6.3
	OD-PABA	5.67	9.73	87.8	7.2	54.2	97.4	9.1
	EHMC	6.68	11.2	95.9	8.1	54.6	96.3	8.1
Effluent wastewater	BP-3	3.22	7.98	97.1	8.4	51.5	96.8	7.5
	OD-PABA	3.52	8.05	94.5	7.2	52.3	97.7	8.1
	EHMC	4.23	8.84	95.8	9.1	53.1	97.9	8.7

a) ND, Not detected or lower than LOD.

Table 3

Comparison of the current method with other methods for extraction and determination of UV filters.

Instrumentation[a]	T (min)	Linear ranges ($\mu g \cdot L^{-1}$)	LOD ($\mu g \cdot L^{-1}$)	RSD (%)	Recovery (%)	Refs
C_{18}-SPE-LC-DAD	~30	0.02-0.2	0.014[b]	2.8	95.0-97.0	[39-40]
IL-SDME-LC-UV	37	1-150	0.07-0.19	2.8-7.9	96.0-110	[41]
IL-HF-LPME-HPLC-UV	50	5-1000	0.2-0.5	1.1-8.4	95.2-105	[42]
IL-DLLME-HPLC-UV	10	0.5-500	0.06-0.16	2.8-7.6	92.8-114	[43-44]
PDMS-SPME-GC-FID	45	10-500	0.87-2.47[b]	4.5-7.9	82.0-98.0	[37-45]
C_{12}-SPME-HPLC-UV	60	5-200	0.69-1.37	0.6-1.9	69.7-102	[46]
TiO_2-SPME-HPLC-UV	30	0.1-400	0.026-0.089	4.5-9.6	88.8-107	[16]
Zn-ZnO-SPME-HPLC-UV	40	0.1-200	0.032-0.064	5.5-8.3	96.3-102	This method

[a] C_{12}, dodecyl; C_{18}, octadecyl; DAD, diode array detection; FID, flame ionization detection; IL, ionic liquid; TiO_2, titanium oxide.

[b] Limit of quantification.