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PAPER

Octadecyltrimethoxysilane functionalized ZnO nanorods as a novel coating for solid-phase microextraction with strong hydrophobic surface†

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In this paper, we have, for the first time, proposed an approach by combining self-assembled monolayers (SAMs) and nanomaterials (NMs) for the preparation of novel solid-phase microextraction (SPME) coatings. The self-assembly of octadecyltrimethoxysilane (OTMS) on the surface of ZnO nanorods (ZNRs) was selected as a model system to demonstrate the feasibility of this approach. The functionalization of OTMS on the surface of ZNRs was characterized and confirmed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The OTMS-ZNRs coated fiber exhibited stronger hydrophobicity after functionalization, and its extraction efficiency for non-polar benzene homologues was increased by a factor of 1.5–3.6 when compared to a ZNRs fiber with almost identical thickness and façade. In contrast, the extraction efficiency of the OTMS-ZNRs coated fiber for polar aldehydes was 1.6–4.0-fold lower than that of the ZNRs coated fiber, further indicating its enhanced surface hydrophobicity. The OTMS-ZNRs coated fiber revealed a much higher capacity upon increasing the OTMS layer thickness to 5 μm, leading to a factor of 12.0–13.4 and 1.8–2.5 increase in extraction efficiency for the benzene homologues relative to a ZNRs coated fiber and a commercial PDMS fiber, respectively. The developed HS-SPME-GC method using the OTMS-ZNRs coated fiber was successfully applied to the determination of the benzene homologues in limnetic water samples with recovery ranging from 83 to 113% and relative standard deviations (RSDs) of less than 8%.

Introduction

Since its inception in 1990,[1] solid-phase microextraction (SPME) has been widely applied to the extraction of analytes of interest in the environment,[2] food,[3] pharmaceuticals[4] and biological fluids[5] because of its sensitivity, rapidity, simplicity, being free of solvents and having the feasibility to couple with routine analytical instruments, predominantly GC and HPLC.[6] Traditionally, the SPME technique is based on the partitioning of analytes between the sample and the fiber coated with a stationary phase, *i.e.* coating. It is well-known that the nature of SPME coatings determines the extraction performance, and so many recent researches on SPME have been focused on the preparation and characterization of new sorbents with remarkable chemical and mechanical stability, enhanced sensitivity and selectivity for specified analytes.[7] In the last two decades, many sorbents, such as sol–gel coatings,[8] electrochemical polymers,[9] molecular imprinted polymers[10] and nanomaterials (NMs),[11] have been successfully explored as SPME coatings. Among these sorbents, NMs have lately attracted great attention due to their unique electronic and chemical properties as well as the large surface area-to-volume ratio.[11] The research group of Jiang has prepared well-aligned TiO_2 nanotubes *in situ* on a Ti wire as a novel SPME coating.[11b] This coating exhibits many advantages over commercial SPME fibers, including high rigidity, good chemical stability, large surface areas (high adsorptivity) and good selectivity for PAHs and alkanes. Subsequently, they reported a gold nanoparticles (NPs) coated SPME fiber, which possessed superb selectivity to the extraction of PAHs with larger π systems probably due to the large relativistic effect of Au.[11c] Very recently, Zhang and co-workers have developed a chemically bonded graphene coated fiber using 3-aminopropyltriethoxysilane as the cross-linking agent. The high surface-to-volume ratio, hydrophobic surface and rich π-stacking electrons are attributed to its excellent adsorption affinity for the PAHs.[11e]

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The self-assembled monolayer (SAM), a well-ordered monomolecular layer formed spontaneously by the reaction of certain types of molecules with supporting solid materials, has gained extensive acceptance to modulate the surface properties for a variety of applications, such as sensors and biochips, fuel cells, biomaterials and molecular electronics.[12,13] In the broadest sense, some self-assembled systems prone to multilayers could be classified as SAMs.[13] Organosilane-based monolayers are possibly the most commonly exploited self-assembled systems.[13] Several organosilanes, such as octadecyltrimethoxysilane (OTMS), octadecyltriethoxysilane (OTES) and octadecyltrichlorosilane (OTCS) have been successfully self-assembled on various substrates, including silicon oxide, aluminium oxide, titanium oxide, quartz, glass, mica, zinc selenide and gold.[14] Watts *et al.* reported the fabrication of a ZnO surface using γ-(aminopropyl)triethoxysilane (γ-APS), by which the bonding to the ZnO preferentially occurred *via* the amino group.[15] Allen *et al.* utilized OTES as an organosilane with the aid of a catalyst (*n*-butylamine) to functionalize the ZnO surface *via* covalent Si–O bonding.[16] After functionalization, the contact angles transformed from approximately 17° to 106°, confirming the formation of a very stable hydrophobic surface.

These studies reveal to us that the fabrication of SAMs on the surface of NMs would be suitable for the preparation of SPME coatings. By this approach, the surface properties of NMs such as biocompatibility, polarity and conductivity could be readily fine-tuned using SAMs with different functionalities. On the other hand, the orientation and the high surface-to-volume ratio of the NMs could still be reserved after functionalization. However, to the best of our knowledge, no effort has been devoted to the utilization of SAMs on NMs as a novel SPME coating so far.

ZnO NMs, particularly one-dimensional ZnO nanorods (ZNRs) and nanowires, have shown tremendous significance in many fields, such as short-wavelength nanolasers, solar cells, piezoelectronic nanogenerators and nanosensors, due to their wide bandgap, specific electrical property, and excellent chemical and thermal stability.[17] More importantly, compared to other NMs, ZnO NMs are easier to prepare with low cost. Besides that, they could be deposited on various substrates with well-aligned orientation. Thus far, ZNRs and ZnO nanotubes-based SPME coatings have been prepared and applied to headspace SPME (HS-SPME) of volatile or semi-volatile organic compounds.[18] In these studies, well-aligned ZnO NMs were prepared and their high surface-to-volume ratios were proven to play a crucial role in the analyte extraction.

Herein, based on the above discussions, an organosilane-based SAM functionalized on the surface of ZNRs was selected as a typical example to prepare a novel SPME coating. Firstly, we directly synthesized ZNRs on the surface of a stainless steel wire using a one-step hydrothermal process. Subsequently, we functionalized the ZNRs using OTMS as a silanization reagent and *n*-butylamine as a catalyst. Using this approach, we, for the first time, prepared OTMS-ZNRs on a stainless steel wire as a novel SPME coating. Typical non-polar (five benzene homologues) and polar (five aldehydes) compounds were used as test compounds to evaluate thoroughly the extraction performance of the OTMS-ZNRs SPME coating.

Experimental

Modification of stainless steel wire substrate

In order to protect the fiber coating from being shaved by the SPME holder, a modification of the stainless steel wire substrate was carried out by introducing a guiding tube. The modification procedure was similar to that detailed in our previous report,[18d] and a schematic diagram of the modification procedure was presented in Fig. S1.† Specifically, a 1.2 cm hollow stainless steel tube was fixed on the end of a stainless steel wire (14.8 cm) using adhesive. The other end of the hollow tube was fixed with a 1.0 cm stainless steel wire, which was used for coating. The diameter of the hollow stainless steel tube matched with the diameter of the stainless steel wires and the inner diameter of the SPME holder needle. Using this approach, the stainless steel tube functioned as a guiding tube since it ensured the coated stainless steel wire position in the middle of the SPME holder needle. The modified stainless steel wires were used as the substrate for the ZNRs and OTMS-ZNRs coating.

Preparation of ZnO nanorod coated fiber

The ZNRs growth solution was prepared by modifying the method reported by Vayssieres *et al.*[19] The preparation of the ZNRs coated fiber included the following processes: (1) before being coated, the modified stainless steel wires (17 cm) were successively cleaned with acetone and ethanol in an ultrasonicator for 10 min, then washed with ultrapure water and finally dried at room temperature; (2) a 20 mL aqueous solution of equal amounts (0.025 mol L^{-1}) of $Zn(NO_3)_2 \cdot 6H_2O$ and hexamethylenetetramine (HMT) was ultrasonically mixed in a glass bottle. Several modified stainless steel wires were used to penetrate through a foam cap, and a length of approximately 1.0 cm was left in the end for coating; (3) the foam cap with the stainless steel wires was embedded into the glass bottle, and the stainless steel wires remained immersed in the solution for 4 h at 90 °C. Finally, the ZNRs coated fibers were rinsed using water and then dried in an oven for 2 h.

Preparation of OTMS-ZNRs coated fiber

The monolayer of OTMS on the surface of the ZNRs coated fiber was prepared based on the methods proposed by Allen *et al.*[16] The silanization solution was prepared by adding, in sequence, 10 mL toluene, 300 μL OTMS and 150 μL *n*-butylamine to a 20 mL flask. The as-obtained solution was mixed homogenously with stirring. A ZNRs coated fiber was slightly wetted by water, and then it was perpendicularly dipped into the mixed solution, which was agitated at the stirring rate of 200 rpm. The reaction proceeded at room temperature for 24 h. After reaction, the as-prepared OTMS-ZNRs coated fiber was pulled out, and sequentially washed with toluene, acetone and water to eliminate the residual non-bonding OTMS, and finally placed in an oven at 110 °C for 4 h. The OTMS layer with 5 μm thickness on the surface of the ZNRs coated fiber was prepared as in the same procedure mentioned above, except that the composition of the silanization solution contained 10 mL ethanol, 300 μL OTMS, 500 μL water and 150 μL *n*-butylamine. The ZNRs and

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OTMS-ZNRs coated fibers were mounted into a laboratory-made SPME holder modified from a 5 μL micro-syringe.[20]

HS-SPME procedure

The sample vial containing the standard solution of benzene homologues or aldehydes was clamped and placed on a magnetic stirrer. The needle of the SPME holder pierced the Teflon-lined septum, and then the OTMS-ZNRs (or ZNRs) fiber coating was pushed out and hung above the sample solution (0.5 cm). The HS-SPME procedure for the benzene homologues and aldehydes was performed under stirring (600 rpm) at 30 °C for 20 min and 45 °C for 15 min, respectively. After extraction, the fiber was withdrawn in the SPME holder and inserted into the GC injector.

Real water analysis

The limnetic water samples were collected from a pond on the campus of Xiamen University and the YunDang Lake located north of Xiamen city. All the water samples were filtered using microfiltration membranes (0.45 μm). After filtration, approximately 6.25 g NaCl was weighed and added to 25 mL of the water samples to make the salinity *ca.* 0.25 g mL^{-1}. The following HS-SPME procedure was the same as that mentioned in the last section.

Results and discussions

The characterization of ZNRs and OTMS-ZNRs fiber coating

To achieve a larger surface-to-volume ratio of ZNRs, several parameters, including the precursor concentration, reaction time and reaction temperature, were optimized during the synthesis procedure. Based on our previous results,[18d] the precursor concentrations of $Zn(NO_3)_2 \cdot 6H_2O$ and HMT were chosen as 0.025 mol L^{-1}. The reaction temperature and time were set at 90 °C and 4 h. Under these optimized conditions, well-oriented ZNRs were successfully synthesized on the surface of stainless steel wires. As displayed in Fig. 1a and b, dense ZNRs were homogenously deposited on the surface of the stainless steel wire, and all of them possessed similar diameter and length. It can be seen from Fig. S2† that a majority of the ZNRs belong to hexagonal array, and the diameters primarily distribute in the range of 300–500 nm with the length (*i.e.* coating thickness) about 5 μm.

An established organosilane-based SAM system, in which OTMS was self-assembled on the ZnO surface, was adopted and prepared based on the method proposed by Allen *et al.*[16] The silanization solution was composed of toluene, OTMS and *n*-butylamine, which functioned as solvent, silanization reagent and catalyst, respectively. The addition of *n*-butylamine was proven to be able to promote the covalent Si–O bond formed between OTMS and the ZnO surface, although the mechanism of this modification method was not completely understood.[16] The intermolecular and substrate–molecular interaction was not the major concern and was not discussed in detail here. The morphology of the OTMS-ZNRs coated fiber was characterized using SEM. It could be seen from Fig. 1c and d that the morphologies of the OTMS-ZNRs were similar to those of ZNRs except for an imperceptible layer covering the surface of the ZNRs, indicating that the effective surface area was well reserved after functionalization. The results from EDS analysis (Fig. S3† and Table S1†) showed that the atom content of silicon and carbon in the OTMS-ZNRs was 0.25% and 29.04%, further verifying that an ultrathin OTMS layer was successfully fabricated on the surface of the ZNRs. It is worth noting that the OTMS-ZNRs coating was washed thoroughly with toluene,

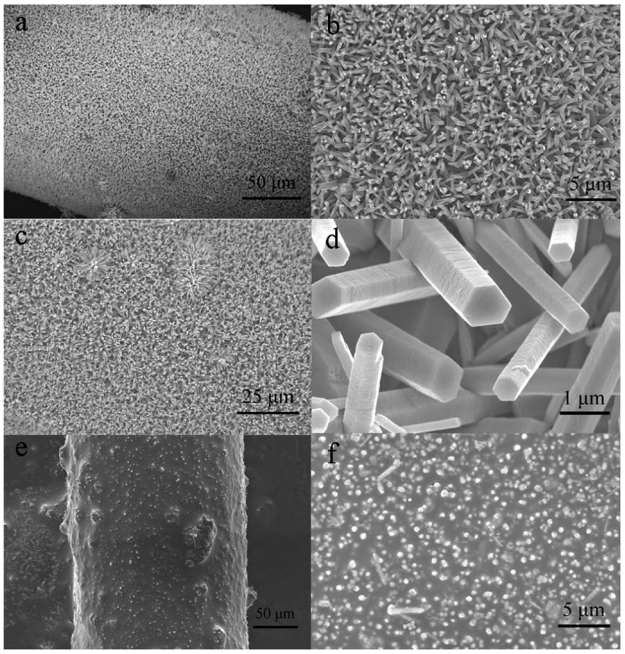

Fig. 1 SEM images of the ZNRs coated fiber at (a) 400× magnification, and (b) 4000× magnification; the OTMS-ZNRs coated fiber (monolayer) at (c) 800× magnification, and (d) 20 000× magnification; and the OTMS-ZNRs coated fiber (5 μm) at (e) 400× magnification, and (f) 4000× magnification.

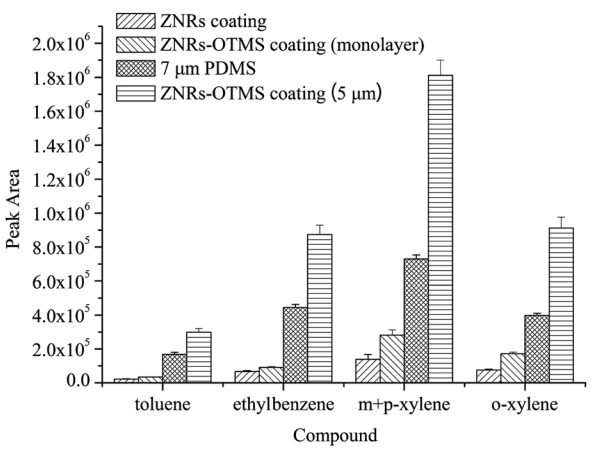

Fig. 2 Comparison of extraction amounts of the benzene homologues using a ZNRs coated fiber, commercial 7 μm PDMS fiber and OTMS-ZNRs coated fiber. Conditions: sample volume, 25 mL; stirring rate, 600 rpm; extraction temperature, 30 °C; salt concentration, 0.25 g mL^{-1}; extraction time, 20 min; desorption temperature, 220 °C; desorption, 0.5 min. Concentration of each analyte, 2 μg mL^{-1}. The error bar shows the standard deviation (SD) of triplicate extractions.

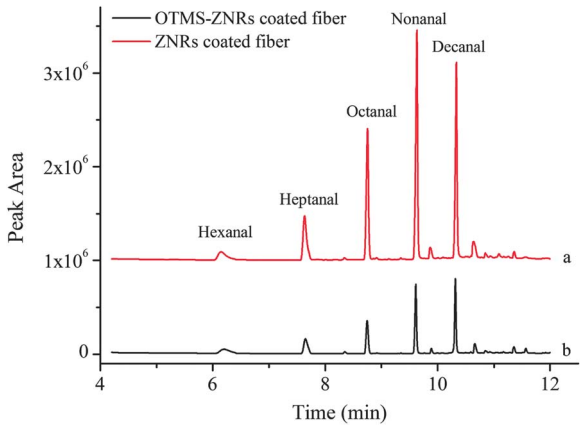

Fig. 3 GC chromatograms obtained for the analysis of aldehydes using a ZNRs coated fiber (a) and an OTMS-ZNRs coated fiber (b). Conditions: sample volume, 5 mL; stirring rate, 600 rpm; extraction temperature, 45 °C; extraction time, 15 min; desorption temperature, 220 °C; desorption, 1 min. Concentration of each analyte, 10 μg mL^{-1}.

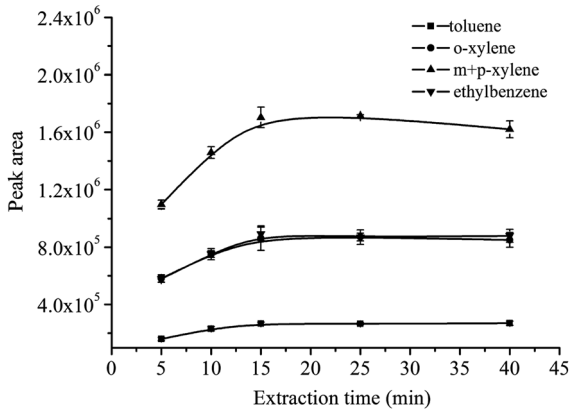

Fig. 4 The effect of extraction time on HS-SPME efficiency for the benzene homologues. Other conditions as in Fig. 2. The error bars show the SD of triplicate extractions.

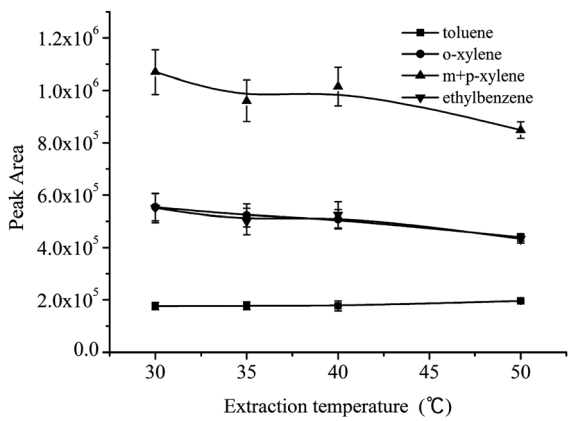

Fig. 5 The effect of extraction temperature on HS-SPME efficiency for the benzene homologues. Other conditions as in Fig. 2. The error bars show the SD of triplicate extractions.

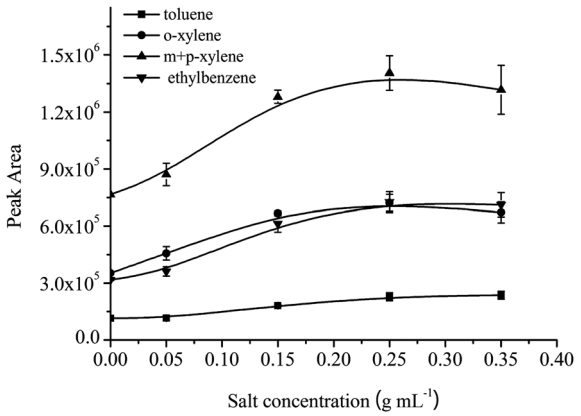

Fig. 6 The effect of salt concentration on HS-SPME efficiency for the benzene homologues. Other conditions as in Fig. 2. The error bars show the SD of triplicate extractions.

acetone and water to eliminate the non-bonded residual OTMS on the surface of the ZNRs. In this application, whether a well-packed monolayer, or rather an ill-defined multilayer is formed, is not virtually a significant issue. As a consequence, further experiments were not conducted for the characterization of the OTMS-ZNRs coating.

As discussed above, the surface of the OTMS-ZNRs should exhibit stronger hydrophobicity than that of ZNRs without changing the orientation and arrangement of the ZNRs. Consequently, the OTMS-ZNRs coated fiber is supposed to show a higher affinity for non-polar compounds than that of the ZNRs coated fiber. Typical non-polar compounds, several benzene homologues, including toluene, ethylbenzene, *o*-xylene, *p*-xylene and *m*-xylene, were selected as model compounds to test the extraction performance of the OTMS-ZNRs coated fibers. As displayed in Fig. 2, the extraction efficiency of a ZNRs coated fiber for the benzene homologues was rather low, probably due to its hydrophilic surface.[16,21] It should be noted that the chromatographic peaks of *p*-xylene and *m*-xylene overlapped completely, and so they were quantified together as a peak. After functionalization, the extraction efficiency of the OTMS-ZNRs coated fiber for the benzene homologues was increased by a factor of 1.5–3.6 compared to that of the ZNRs coated fiber. In addition, a subtle detail was noticed in that the extraction of the OTMS-ZNRs coated fiber for methanol (used as the solvent for the preparation of stock solutions and known as polar) was obviously suppressed compared to that of the ZNRs coated fiber. It should be emphasized again that the OTMS-ZNRs and ZNRs fiber coating used for this comparison are of nearly identical length and façade. These results verified the above hypothesis that the SAM of OTMS made the surface of the ZNRs more hydrophobic and thus improved its extraction efficiency for the non-polar compounds.

In contrast, it is logical that the OTMS-ZNRs coated fiber is supposed to show lower affinity towards polar compounds. In our previous report, we have proved that the ZNRs coated fiber exhibited excellent extraction efficiency towards polar aldehydes.[18d] In this study, five aldehydes were selected as model polar compounds for comparison of the extraction efficiency of the ZNRs and OTMS-ZNRs coated fiber. Fig. 3 shows that the

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Table 1 Linear equation, linear range, determination coefficients, limits of detection ($S/N = 3$) and repeatability of the proposed HS-SPME-GC method[a]

Analyte	Correlation coefficient (r)	Linear range/μg mL^{-1}	LOD/ng mL^{-1}	Repeatability (%)	Reproducibility (%)
Toluene	0.9989	0.10–10	5.5	5.9	12.5
Ethylbenzene	0.9995	0.05–10	3.4	4.1	9.6
m,*p*-Xylene	0.9993	0.05–10	4.1	9.6	15.4
o-Xylene	0.9990	0.05–10	1.5	7.6	13.6

[a] Experimental conditions as in Fig. 2.

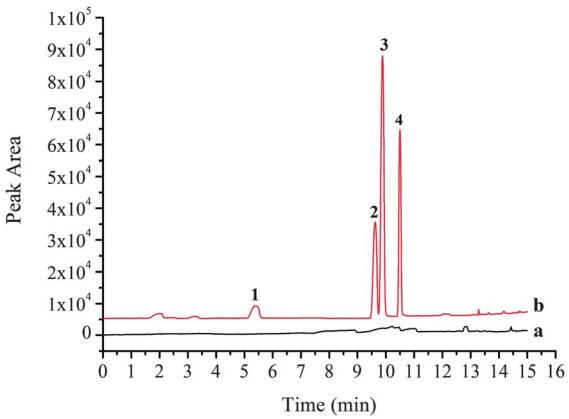

Fig. 7 GC chromatograms obtained using the HS-SPME-GC method for the analysis of (a) YunDang pond water and (b) YunDang pond water spiked with 1 μg mL^{-1} of each analyte. Experimental conditions as in Fig. 2. Peak identity: 1, toluene; 2, ethylbenzene; 3, *m*+*p*-xylene; 4, *o*-xylene.

extraction efficiency of the ZNRs coated fiber for aldehydes was 1.6–4.0-fold higher than that of the OTMS-ZNRs coated fiber, demonstrating its decreased surface polarity after the OTMS functionalization. All of these results confirmed the successful functionalization of OTMS and the accompanying enhanced surface hydrophobicity.

In view of the strong hydrophobicity of the OTMS, further increase of its layer thickness may be advantageous for the extraction of the OTMS-ZNRs coated fiber towards benzene homologues. In order to increase the OTMS layer thickness, water was introduced into the silanization solution, since it has been proved to be able to facilitate the silanization process.[16] Ethanol was used for the substitution of toluene as the solvent to dissolve all the solutes. The silanization process was observed to be drastic, since a white precipitate was formed during the reaction. As the functionalization time increased, the OTMS layer thickness was found to increase correspondingly. At the functionalization time of 24 h (Fig. 1e and f), the rough outline of the ZNRs was reserved even if the main bulk was covered by the OTMS layer, and the thickness was about 5 μm. In this study, further attempt to increase the OTMS layer thickness was not carried out, since this may lead to complete coverage of the ZNRs and probably lengthens the equilibrium time for the extraction of the target analytes. Thus, the OTMS-ZNRs fiber coating with a 5 μm thickness of the OTMS layer was used for further study. As expected, when the thickness of the OTMS layer was increased to 5 μm, the extraction efficiency of the OTMS-ZNRs coated fiber for each benzene homologue was significantly higher (12.0–13.4-fold) than that obtained using the ZNRs coated fiber (Fig. 2). In order to further evaluate the extraction ability of the OTMS-ZNRs coated fiber, a commercial 7 μm PDMS coated fiber was selected for comparison due to its similar coating thickness. The results (Fig. 2) revealed that the OTMS-ZNRs coated fiber still showed 1.8–2.5-fold as high extraction efficiency as that of the commercial fiber, further confirming its excellent extraction ability for the benzene homologues after the functionalization.

Optimization of the HS-SPME for the benzene homologues

In order to obtain the maximum extraction efficiency of the OTMS-ZNRs coated fiber for the benzene homologues, several parameters including extraction time, extraction temperature, ionic strength, stirring rate, desorption temperature and desorption time were optimized.

Table 2 The recoveries of the proposed HS-SPME-GC method for the analysis of benzene homologues in limnetic water samples[a]

	Spiked concentration/μg mL^{-1}	Recovery ± RSD (%)			
		Toluene	Ethylbenzene	*m*,*p*-Xylene	*o*-Xylene
Pond water	0.5	113 ± 5	98 ± 7	108 ± 8	109 ± 3
	1	93 ± 8	88 ± 2	92 ± 4	93 ± 2
	5	95 ± 3	90 ± 1	92 ± 2	94 ± 6
Lake water	0.5	102 ± 5	93 ± 7	99 ± 6	107 ± 5
	1	93 ± 7	86 ± 2	87 ± 1	87 ± 3
	5	85 ± 4	83 ± 4	83 ± 4	86 ± 8

[a] Experimental conditions as in Fig. 2.

The extraction time profile was established by plotting the peak areas of the benzene homologues *versus* the extraction time. The extraction time was investigated at 5, 10, 15, 25 and 40 min, and Fig. 4 shows that the extracted amounts of the analytes increased as the time was increased from 5 to 15 min and tended to remain unchanged thereafter, revealing the achievement of equilibrium. This short equilibrium time was mainly attributed to the thin thickness (*ca.* 5 μm) and high surface-to-volume ratio of the OTMS-ZNRs coating. In the SPME technique, the extraction at equilibrium is beneficial for the improvement of method precision.[22] To ensure that the SPME was performed at equilibrium, an extraction time of 20 min was adopted for the subsequent experiments.

The extraction temperature always imposes opposite effects on the HS-SPME procedure for the analytes. On the one hand, elevating the temperature accelerates the diffusion of analytes into the headspace, and hence is able to shorten the equilibrium time. On the other hand, an elevated temperature is adverse to the adsorption of analytes on the coating, since adsorption is generally an exothermic process. The extraction temperature effect was investigated in the range from 30 to 50 °C. As shown in Fig. 5, the extracted amounts of the analytes declined slightly as the temperature increased from 30 to 50 °C, except in the case of toluene, which remained almost constant. This phenomenon could possibly be explained by the fact that the selected benzene homologues are extremely volatile and readily diffuse from sample matrix to the headspace at a low temperature. Higher temperature contrarily decreases the partition coefficient of the analytes in the coating. In the following experiments, the extraction temperature was set at 30 °C.

In HS-SPME, analytes initially diffuse into the headspace and then partition into the fiber coating. Agitation is recognized to facilitate the mass transfer rate of analytes from the sample matrix into the headspace, which is favorable for the extraction equilibrium. Based on the results obtained, the chromatographic peak areas for the analytes changed little with the variation of stirring rate, possibly due to the fast extraction equilibrium. In consequence, a moderate stirring rate of 600 rpm was chosen.

Addition of inorganic salt, such as sodium chloride and sodium sulfate, is well-known to be able to decrease the solubility of analytes in the sample matrix, leading to a higher extraction efficiency. In this study, different amounts of sodium chloride were added to the sample solution making the final salinity in the range 0–0.35 g mL^{-1}. As indicated in Fig. 6, the extracted amounts of the analytes increased as the salinity increased from 0 to 0.25 g mL^{-1}. Further increase of salinity scarcely imposes any positive effect on the extraction efficiency, and thus the salinity was chosen as 0.25 g mL^{-1}.

Effective desorption is crucial for obtaining analytes with good chromatographic peak shape as well as ensuring no carry-over effect. The desorption temperature and time were both optimized. Considering the volatility of the selected benzene homologues, the desorption temperature was adjusted to 180, 200, 220, 240 and 260 °C, and the desorption time was fixed at 2 min. The results revealed that the chromatographic peak areas of the analytes remained almost constant in the temperature range studied, indicating the complete desorption of the benzene homologue even at 180 °C. To ensure complete desorption of the extracted analytes efficiently, the desorption temperature was set at 220 °C.

Suitable desorption time was another key factor for effective desorption. In principle, an insufficient desorption time results in incomplete desorption and a carry-over effect, whereas a prolonged desorption time causes peak broadening and poor resolution. At a sufficiently high temperature, the desorption time was dependent on the thickness of the fiber coating. As a general rule, the adsorbed analytes are easier to release from the fiber coating with a thinner thickness. The desorption time was investigated at 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 min. It was found that the benzene homologues could be completely desorbed at 220 °C within 1 min. This short desorption time was ascribed to the small thickness and the high surface-to-volume ratio of the fiber coating. However, a desorption time equal to or more than 1 min was found to make the chromatographic peaks of ethylbenzene and *m*-,*p*-xylene overlap partly. Consequently, to obtain chromatographic peaks with better resolution, the desorption time was set to 0.5 min with splitless mode, while the fiber coating was still placed in the GC injector for another 2 min with split mode. This procedure was carried out to ensure no carry-over effect.

Analytical data of the HS-SPME-GC method

Under the optimized conditions, the analytical parameters including linear equation, determination coefficient, linear range and limits of detections (LODs) were studied and the data were listed in Table 1. The chromatographic peak areas were linear with the concentration spanning from 0.05 to 10 μg mL^{-1} for all benzene homologues with a correlation coefficient (r) larger than 0.999, except in the case of toluene from 0.1 to 10 μg mL^{-1} with $r = 0.9989$. Triplicate analysis of blank water samples was carried out using the proposed HS-SPME-GC method for the determination of the limits of detection. The LODs, defined at a signal-to-noise of 3 ($S/N = 3$), were in the range of 1.5–5.5 ng mL^{-1}. The repeatability of a single fiber was evaluated based on the analysis of a standard mixture at 1 μg mL^{-1} with 6 replicates, and the relative standard deviations (RSDs) for the benzene homologues ranged from 4.1 to 9.6%. The fiber-to-fiber reproducibility was studied using four OTMS-ZNRs coated fibers prepared in the same batch, and the RSDs ranged between 9.6 and 15.4%. Based on the experimental results, the OTMS-ZNRs coated fiber could be used for more than 80 times without any obvious decline in extraction ability. This was mainly attributed to the fact that the modified stainless steel wires with the guiding tube effectively protected the fiber coating from shaving and therefore prolonged its lifetime.

Application to real samples

To evaluate its applicability to the analysis of environmental water samples, the established HS-SPME-GC method using the OTMS-ZNRs coated fiber was used to analyze benzene homologues in locally collected limnetic water samples. No detectable benzene homologues could be found in the limnetic water samples. For the sake of determining the method reliability, limnetic water samples spiked at three concentration levels (0.5, 1 and 5 μg mL^{-1}) were also used for recovery experiments. The analytical results are summarized in Table 2. As shown in Table 2, the recoveries for the benzene homologues were 93–113% at 0.5 μg mL^{-1}, 86–93% at 1.0 μg mL^{-1} and 83–95% at 5 μg mL^{-1},

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respectively. These recovery data were obtained based on triplicate analysis for each concentration level, and the RSDs were less than 8%. Fig. 7 shows typical chromatograms of a limnetic water sample collected from the YunDang Lake and its spiked solution at 1 μg mL^{-1}.

Conclusions

In summary, a novel approach by combining the SAMs and NMs was proposed for the preparation of SPME coatings. A ZNRs coated stainless steel wire was utilized as the substrate for the functionalization of OTMS, in view of its high surface-to-volume ratio, easy preparation and chemical and mechanical stability. After functionalization, the stronger hydrophobicity of the OTMS-ZNRs coated fiber was verified by the fact that it shows higher and lower extraction efficiency for the non-polar benzene homologues and polar aldehydes compared to that of a ZNRs coated fiber. This study prompts us that various SAMs could be specially applied for the surface functionalization of NMs, such as TiO_2 nanotubes, gold NPs, carbon nanotubes and graphene. For example, diverse thiols with different terminal functional groups could be easily self-assembled onto the surface of gold NPs *via* the strong gold–thiolate (Au–S) bond. We believe that, using this approach, various SPME coatings with featured surface characteristics could be potentially obtained.

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