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High-efficiency solid-phase microextraction performance of polypyrrole enhanced titania nanoparticles for sensitive determination of polar chlorophenols and triclosan in environmental water samples†

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In this work, a polypyrrole (PPy)/TiO_2 nanocomposite coating was fabricated by the direct electropolymerization of pyrrole on annealed TiO_2 nanoparticles and evaluated as a novel direct immersion solid phase microextraction (DI-SPME) fiber coating for extraction of trace amounts of pollutants in environmental water samples. The functionalized fiber is mechanically and chemically stable, and can be easily prepared in a highly reproducible manner. The effects of the pyrrole monomer concentration, polymerization voltage and polymerization time on the fiber were discussed. Surface morphological and compositional analyses revealed that the composite coating of nano polypyrrole and titanium dioxide nanoparticles (TiO_2NP_s) uniformly doped the Ti substrate. The as-fabricated fiber exhibited good extraction capability for phenolic compounds in combination with high performance liquid chromatography-UV detection (HPLC-UV). At the optimum SPME conditions, the calibration curves were linear ($R^2 \geq 0.9965$). LODs and LOQs of less than 0.026 μg L^{-1} and 0.09 μg L^{-1}, respectively, were achieved, and RSDs were in the range 3.5–7.2%. The results obtained in this work suggest that PPy/TiO_2 is a promising coating material for future applications of SPME and related sample preparation techniques.

1. Introduction

Phenolic compounds are widely used in chemical industry production processes, such as in disinfectants, wood preservatives, plastics, dyes, pesticides, paper and petrochemical products.[1–5] Consequently, phenolic compounds can be detected in environmental water, soil and sediment.[6–8] Most phenolic compounds are highly toxic, are not very biodegradable, can cause cancer, abnormalities and mutations, and can accumulate in organisms, with potentially serious impacts on the human endocrine system.[9,10] Since the concentration levels of phenolic compounds are generally low in complex matrices, the development of simple, efficient and selective preconcentration and separation techniques for phenolic pollutants in environmental water is highly desirable to achieve reliable results.[11]

High-performance liquid chromatography (HPLC) is frequently used to determine phenolic compounds, unlike gas chromatography (GC), it does not lead to the derivatization of compounds.[12,13] However, with regards to sample preparation

and preconcentration steps in phenolic pollutants analysis, solid phase extraction has gradually replaced liquid–liquid extraction, as it avoids the use of a large number of toxic organic solvents. Until now, the literature survey has shown that a variety of SPME fiber coatings such as graphene,[14,15] polysulfone,[16] carbon nanotubes[17–21] and organic polymer have been used in the extraction of phenolic compounds.[22–24] This convenient and solvent-free extraction method is also sensitive, inexpensive and easy to operate. In SPME, the selection and fabrication of the sorbent is a key consideration because it can effect the analytical parameters such as selectivity, affinity and capacity. In order to enhance the adsorption capacity, to improve the removal efficiency, and to increase selectivity to the solid phase, the study of the stability and surface modification techniques of the fiber is necessary.[25–31]

Electrochemical polymerization is a unique method for the formation of coatings, it has the advantages of a simple preparation process, low cost and good reproducibility.[32–34] Among the conducting polymers, polypyrrole (PPy) is an intrinsic conductive polymer with a long-range π–π conjugation structure. PPy is a widely researched polymer because of its good electrical conductivity, facile synthesis, good environmental stability in ambient conditions, and fewer toxicological problems over many other conductive polymers. Besides all these

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advantages, PPy coatings are mechanically resistant with excellent adhesion to metal substrates especially when applying electrochemical methods. The utilization of PPy as a coating material in SPME has been reported previously for the extraction of organic compounds.[35–38] TiO_2 nanoparticles (TiO_2NPs) are well-defined nanomaterials with large specific surface area, high chemical stability, durability, corrosion resistance, and low-toxicity, and they are easily functionalized by incorporation of organic groups. TiO_2NPs have been employed as fiber coatings for the preconcentration and determination of a wide range of organic compounds.[39] In order to develop nanostructured PPy on robust substrates for practical applications, it would be of great technological importance to be able to deposit PPy directly on the desired nanostructured substrate for a particular application in a simple and cost-effective way. The aim of the present work is to fabricate a novel PPy/TiO_2 nanocomposite using a potentiostatic technique used for the first time as fiber coating for SPME in combination with HPLC-UV, and evaluate its application for the extraction and preconcentration of organic substance in water samples. Electrochemical anodic oxidation of titanium wire is a reliable strategy for the direct growth of the nanostructured TiO_2 coating because of its simplicity, controllable morphology and strong reproducibility in fiber fabrication. More titanol groups in TiO_2NPs increase the number of potential reaction centers. In addition, the porous surface structure makes it easier for pyrrole to dope the TiO_2NPs to form a composite nanomaterial.

The selectivity, interaction mechanism and extraction kinetics of the PPy@TiO_2NPs coating were investigated. The effects of various parameters influencing the performance of the extraction are fully discussed in order to achieve the best experimental results. The validation and the application of the developed method are also addressed for the sensitive determination of trace levels of phenolic pollutants in various water samples.

2. Experimental

2.1. Chemicals and reagents

Polypyrrole (PPy) was supplied by Alfa Aesar (Ward Hill, MA, USA) and was distilled under reduced pressure and stored in a dark bottle in a refrigerator before use. Sodium dodecyl sulfate, sodium chloride (NaCl), 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). Certified individual standards of 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 2-(2,4-dichlorophenoxy)-5-chlorophenol (Triclosan, TCS), 2,4,4′-trichlorobiphenyl (PCB-28), 2,4′,5-trichlorobiphenyl (PCB-31), 2,3′,4,4′,5-pentachlorobiphenyl (PCB-118), 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB-153), were obtained from AccuStandard (New Haven, CT, USA). 2-Hydroxy-4-methoxy-benzophenone (BP-3), 2-ethylhexyl 4-(*N*,*N*-dimethylamino)benzoate (OD-PABA), 2-ethylhexyl-4-methoxycinnamate (EHMC), 2-ethylhexyl salicylate (EHS) were supplied by AccuStandard (New Haven, CT, USA). Naphthalene (Nap), phenanthrene (Phe), fluoranthene (Flt), pyrene (Pyr) and benzo[*a*] pyrene (B[*a*]p) were purchased from Aldrich (St. Louis, MO, USA). Stock standard solutions (100 mg L^{-1}) of each compound were prepared in methanol. Working standard solutions were freshly prepared by diluting the stock standard solution with ultrapure water to the required concentration to study extraction performance under different conditions. These solutions were stored in amber bottles in the refrigerator at 4 °C, shielding from light. All other reagents were of analytical grade.

Ti wire (Φ 250 μm, 99.9% in purity) was supplied by the Alfa Aesar (Ward Hill, MA, USA). Commercially available polyacrylate (PA, 85 μm thickness) and polydimethylsiloxane (PDMS, 100 μm thickness) were obtained from Supelco (Bellefonte, PA, USA). A 0.45 μm micropore membrane of polyvinylidene fluoride was purchased from Xingya Purifying Material Factory (Shanghai, China).

2.2. Instrumentation

Anodization of Ti wires was performed with a precise WY-3D power supply (Nanjing, China). TiO_2 nanoparticles were annealed in an air atmosphere at high temperatures in a OTF-1200X tubular furnace with a Prog/Controller (Kejing, Hefei, China). A CHI832D electrochemical analyzer (Chenhua, China) was used for electropolymerization of PPy. The fabricated fibers were characterized by an Ultra Plus microscope (Zeiss, Oberkochen, Germany) with an Aztec-X-80 energy dispersive X-ray spectrometer. SPME was carried out in a DF-101S thermostat with controlled temperature and magnetic stirring (Changcheng, Zhengzhou, China). The analyses were carried out on a Waters 600E multi-solvent delivery system (Milford, MA, USA) equipped with a Waters 2487 dual λ absorbance detector and a Zorbax Eclipse Plus C 18 column (150 mm × 4.6 mm, 5 μm, Agilent, USA). Chromatographic data was processed with a N2000 workstation (Zhejiang University, China). Desorption was performed in a commercially available SPME-HPLC interface (Supelco, PA, USA). Ultrapure water was obtained from a Sudreli SDLA-B-X water purification system (Chongqing, China).

2.3. Preparation of the PPy@TiO_2NPs/Ti fiber

Fabrication of the PPy@TiO_2NPs nanocomposite SPME coating on the Ti wire involved the following processes: (1) Ti wire of length 6.0 cm was used to fabricate the SPME fibers. One end (1.5 cm long) of the Ti wire was rinsed with methanol and ultrapure water in an ultrasonic bath for 5 min, respectively. (2) The cleaned Ti wire was immersed into the electrolyte of ethylene glycol and water (v/v, 1 : 1) containing NH_4F of 0.5% (w/v) for anodization at 25 V for 60 min at room temperature. TiO_2NPs were formed on the Ti wire *in situ* using Ti wire as the working electrode and a Pt rod as the counter electrode. (3) The TiO_2NPs coating was washed with ultrapure water and then annealed in a quartz tubular furnace at a heating rate of 5 °C min^{-1} up to the preset temperature and held for 2 h. After annealing, the TiO_2NPs coating was then allowed to cool under a nitrogen stream. (4) The composite coating of PPy@TiO_2NPs was synthesized electrochemically *via in situ* polymerization on

the surface of the annealed TiO_2NPs (as the working electrode) from an aqueous solution containing pyrrole and SDS (0.01 M) by applying a constant potential. Thereafter the prepared fiber was washed with acetone and ultrapure water to remove pyrrole monomers in the $PPy@TiO_2NPs$ coating, and dried in vacuum for 3 h at 90 °C. It had been reported in the literature that the introduction of a large counter anion such as anionic surfactants during the preparation of the PPy, leads to improved properties of the polymers.[40,41]

The added SDS will link with TiO_2 *via* sulfonate-like ester bonds, improving the lipophilicity of the surface of TiO_2NPs, and making pyrrole easy to polymerize on its surface. The generated PPy strengthens the bond to inorganic materials, making the polymer difficult to remove. However, high levels of SDS would increase the solution viscosity, resulting in slow ion migration rates under a static state and corresponding reaction rate reduction.

2.4 SPME-HPLC procedure

To examine the extraction capabilities of the fiber, aqueous solutions spiked with the organic compounds were extracted with $PPy@TiO_2NPs/Ti$ fibers using the DI-SPME mode. Prior to use, the fiber was conditioned in methanol for 15 min with an agitation speed of 600 rpm. A 15 mL working standard solution or sample solution was placed into a 20 mL glass vial with a 1 cm magnetic stirrer bar inside, and a polytetrafluoroethylene-coated septa. The SPME fiber was immersed into the heated and stirred sample solution for extraction. Subsequently, the fiber was removed from the sample vial and transferred immediately into the SPME-HPLC interface for static desorption of analytes in the mobile phase. The mobile phase of methanol and water was 70/30, 90/10, 75/25 and 85/15 (v/v) at a flowrate of 1 mL min^{-1} for HPLC analysis of phenolic compounds, PAHs, aromatic amines and UV filters, respectively. The corresponding wavelengths of UV detection were set at 282 nm, 254 nm, 282 nm and 310 nm. To avoid a carryover effect, the fabricated fiber was washed with methanol and ultrapure water for 10 min before the next extraction, respectively.

2.5. Water and waste water samples

A river water sample was freshly collected from the Yellow River (Lanzhou, China). Wastewater (untreated) was sampled from a local wastewater treatment plant. Tap water samples were collected from the university. All water samples were filtered through 0.45 μm micropore membranes to eliminate particulate matter, and then adjusted to pH 7.0 with phosphate buffer, and stored in the refrigerator at 4 °C before analysis.

3. Results and discussion

3.1 Optimization and characterization of electropolymerization

Scanning electron microscopy (SEM) was used to investigate the surface morphology and structure of the $PPy@TiO_2NPs/Ti$ fiber. As compared with the untreated Ti wire (Fig. 1a), the anodized fiber shows a considerably rough microscopic surface (Fig. 1b) and exhibits the randomly oriented nanoparticles coating after anodization. After the anodized fiber was annealed at 550 °C for 2 h under a nitrogen atmosphere, the resulting coating
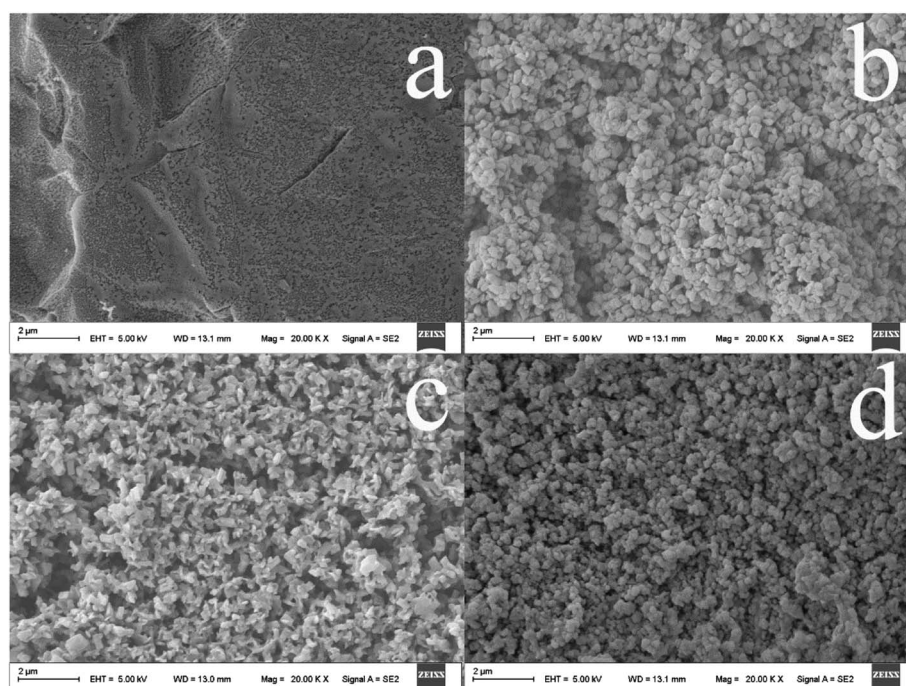

Fig. 1 SEM images of the commercial Ti wire (a), the TiO_2NPs/Ti fiber (b), the annealed TiO_2NPs/Ti fiber (c), and the $PPy@TiO_2NPs/Ti$ coated fiber (d).

possesses a larger surface area, more open access sites, thus providing the desired contact surface area for subsequent strong adhesion of the PPy coating to the TiO_2NPs (Fig. 1c). As can be seen in Fig. 1d, homogeneous PPy was immobilized onto the TiO_2NPs/Ti fiber after electropolymerization of pyrrole and the PPy@TiO_2NPs composite coating was formed on the Ti wire.

3.1.1 Pyrrole. The effects of different concentrations of pyrrole on the structure of the fabricated fiber coatings was studied. The amount of PPy electrodeposited on TiO_2NPs increases with increasing concentration of pyrrole (Fig. 2a–d). As depicted in Fig. 2b, electrodeposition of PPy is homogeneous at lower concentrations of pyrrole. The results show that along with the increase of the pyrrole concentration, PPy size increases, and aggregation occurs, but it is difficult to form the cross-doping polymer coating. When the concentration of pyrrole reached 0.1 mol L^{-1}, the TiO_2NPs were completely covered by PPy, forming a dense deposited film, resulting in a lower specific surface. The surface elements of the fiber were further determined by EDS, and the spectral signal of Ti was hardly observed, which indicates that the TiO_2NPs were completely coated by polypyrrole (Fig. 2d). In the case of 0.05 mol L^{-1} pyrrole, the uniform and compact PPy coating firmly adheres to the TiO_2NPs surface.

3.1.2 Applied voltages. Nucleation, oligomerization and growth of PPy are strongly influenced by applied voltages on different metallic substrates. As shown in Fig. 3, different anodic voltages led to PPy coatings with different morphologies. In this study, a relatively lower voltage was needed for the growth of PPy nanoparticles on the annealed TiO_2NPs fiber. The SEM image of the nanocomposite showed the growth of the homogenous pattern of PPy, which is present in the pores of the TiO_2NPs porous matrix (Fig. 3b). This unique nanostructure results in a much larger surface area, more open access sites and better durability of the as-fabricated fiber. With the increase of voltage (Fig. 3c and d), the pyrrole polymerization reaction was accelerated. High anodic voltages destroy the doped inorganic/organic nanostructures and produce a cauliflower-like PPy coating, resulting in a sharp reduction in the specific surface (Fig. 3d). Therefore 4 V was applied for the electropolymerization of pyrrole on the TiO_2NPs coating.

3.1.3 Polymerization time. Furthermore, the effect of polymerization time on different surface morphology of the fiber was studied. It can be seen in Fig. 4, that only a small amount of pyrrole was polymerized to the surface of TiO_2NPs coating within 20 minutes. With the extension of polymerization time, PPy particles continue to aggregate and grow. However, when the polymerization time exceeded 40 minutes, the interdoped nanostructures of PPy/TiO_2 were gradually replaced by PPy agglomerates (Fig. 4c and d). Therefore, the experiment used 40 minutes as the reaction time to prepare the fiber.

3.2 Surface composition

To find out the reasons for the high affinity of the fabricated fiber to the corresponding target analytes, surface elemental analysis of the Ti wire before and after treatment was performed by energy dispersive X-ray spectroscopy (EDS). As shown in Fig. 5a, the presence of a weak O peak in the EDS spectrum of the commercial Ti wire illustrates the formation of a very thin passivation layer at the surface of the commercial Ti wire.
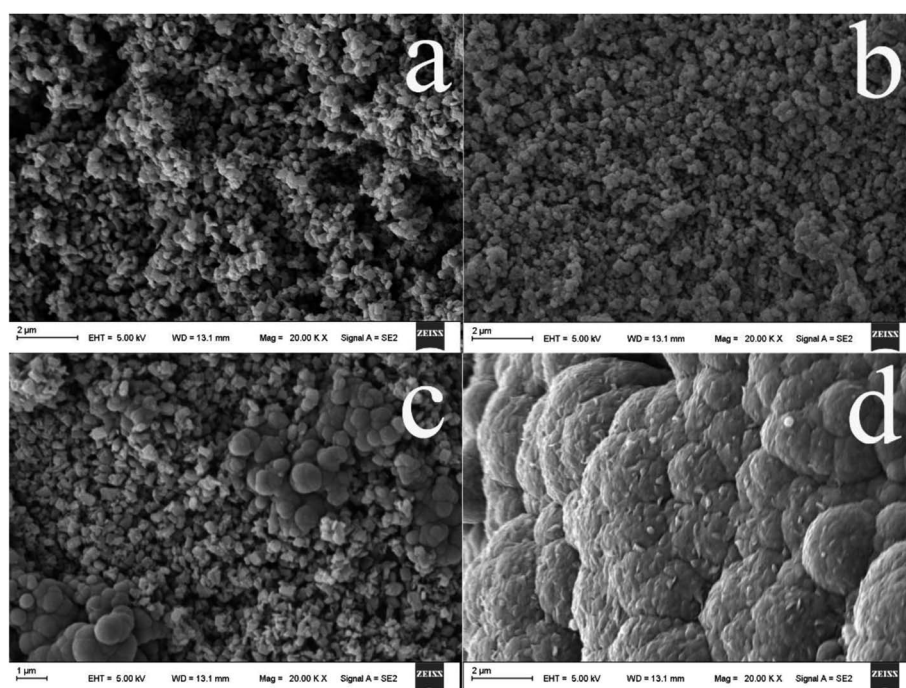

Fig. 2 SEM images of the PPy@TiO_2NPs coating at a pyrrole concentration of 0.02 mol L^{-1} (a), 0.05 mol L^{-1} (b), 0.08 mol L^{-1} (c) and 0.1 mol L^{-1} (d).
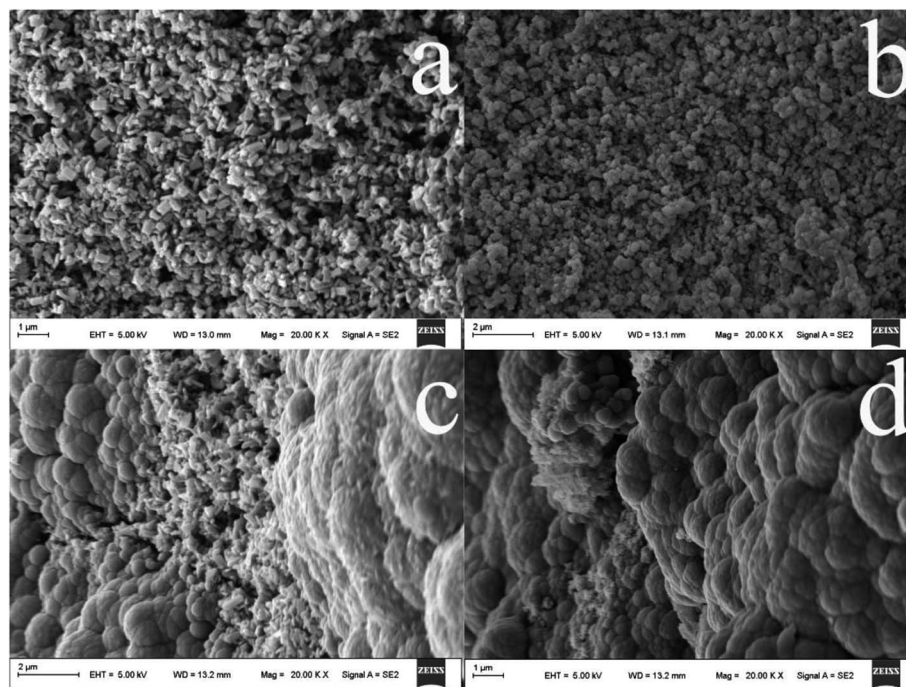
Fig. 3 SEM images of PPy@TiO$_2$NPs at electropolymerization voltages of 2 V (a), 4 V (b), 6 V (c) and 8 V (d).
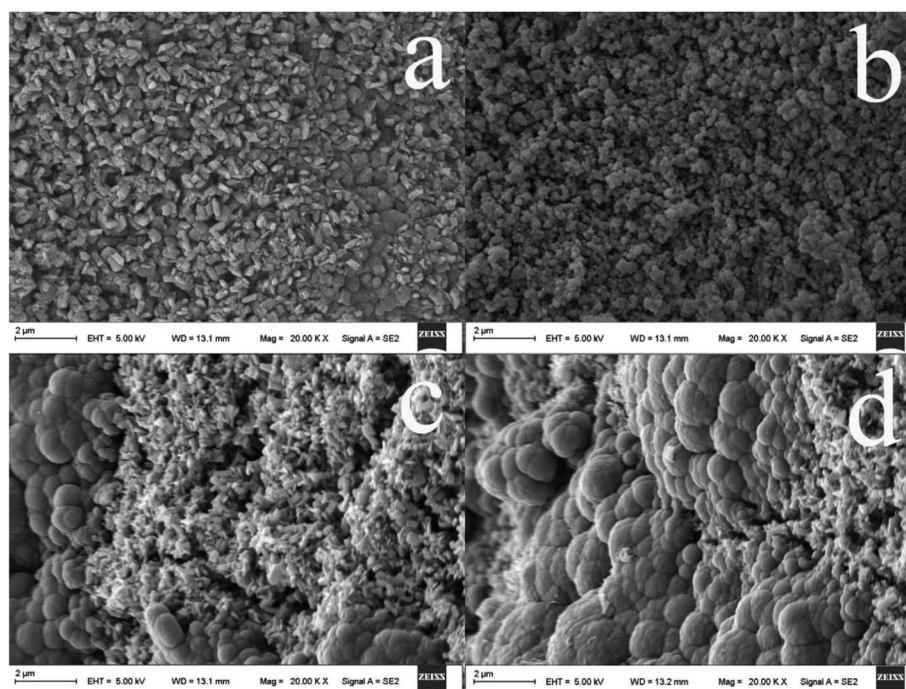
Fig. 4 SEM micrographs of the PPy@TiO$_2$NPs/Ti fiber after polymerization for 20 min (a), 40 min (b), 60 min (c), 80 min (d).

Fig. 5b shows peaks corresponding to the presence of Ti and O. The EDS analysis demonstrates the drastic increase in oxygen content due to the formation of the TiO$_2$NPs coating. As can be seen in Fig. 5c, the mass ratio of O and Ti remarkably decreases after annealing treatment at 550 °C. These phenomena clearly indicate that the Ti–OH was destroyed by dehydration under high temperature annealing, resulting in the reduction of oxygen content (Fig. 5c). After electropolymerization of pyrrole, the signals of C and N elements are observed, as well as those of O and Ti elements (Fig. 5d). Moreover, the atomic percentages of O and Ti elements dramatically decreased with the advent of C and N elements. The molar atomic ratios of Ti to O and C to N
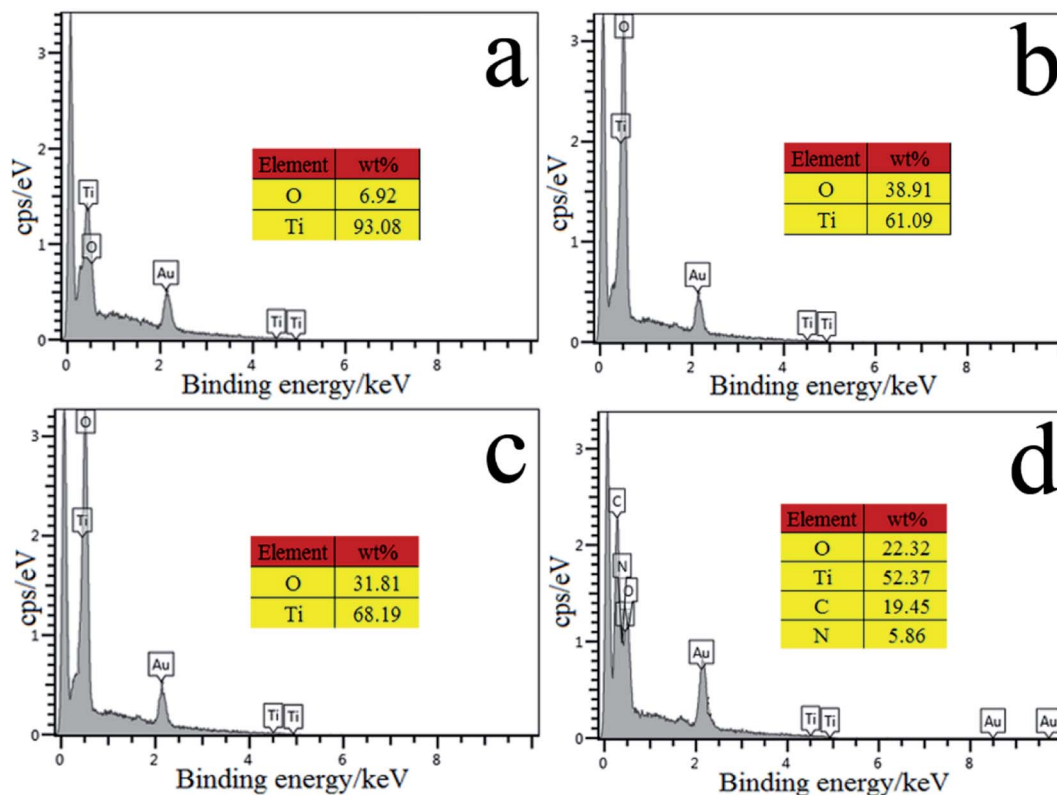
Fig. 5 EDS spectra of the commercial Ti wire (a), the TiO_2NPs/Ti fiber (b), the annealed TiO_2NPs/Ti fiber (c) and the PPy@TiO_2NPs/Ti coated fiber (d).

are almost equal to the stoichiometric ratios of TiO_2 and pyrrole, respectively. This result clearly indicates that a uniform and compact PPy@TiO_2NPs coating was formed, and complete coverage was achieved on the Ti substrate.

3.3. Extractability of the PPy@TiO_2NPs/Ti fiber

The as-prepared SPME fiber coupled with HPLC was then used to extract different polar and structural aromatic compounds including PAHs (Nap, Phe, Flt, Pyr and B[*a*]p), UV filters (BP-3, OD-PABA, EHMC and EHS), PCBs (PCB-28, PCB-31, PCB-118 and PCB-153) and phenolic compounds (2-CP, 2,4-DCP, 2,6-DCP and TCS). It is exciting that the PPy@TiO_2NPs/Ti fiber exhibits excellent extraction capability towards all of the selected organic compounds, especially for phenolic compounds, PAHs and UV filters as shown in Fig. 6.

This special extraction capability may be attributed to the inherent chemical nature of the PPy@TiO_2NPs coating. The surface doped fiber coating retained a large amount of the TiO_2NPs structure. TiO_2 component in the PPy@TiO_2NPs composite coating may have Lewis acid sites on the coating surface, which provides the potential retention of non-polar PAHs, less polar UV filters and PCBs through Lewis acid–base interactions. However, due to the hydrophobicity of the TiO_2, the TiO_2NPs coating allows negligible extraction of hydrophilic phenolic compounds.[42] Pyrrole were immobilized on to the surface of the TiO_2NPs coating *via* electrical aggregation and led to its hydrophilicity, allowing the extraction of polar

compounds by hydrophilic interaction. Furthermore, additional π–π stacking interactions between PPy and aromatic systems may also contribute to the good extraction capability of PPy@TiO_2NPs toward compounds with a larger π–π conjugated structure. The extraction efficiency of phenolic compounds was dramatically improved after surface functionalization. Therefore this novel fiber provides a hopeful approach to effectively extract and analyze trace amounts of chlorophenols and triclosan from complex environmental water samples.

3.4. Optimization of DI-SPME-HPLC-UV conditions

The extraction efficiency of SPME fibers is significantly influenced by extraction conditions. To evaluate the capability of the new fiber, a mixture of four phenolic compounds – 2-CP, 2,4-DCP, 2,6-DCP and TCS – were tested by coupling SPME to HPLC. In order to achieve the optimal extraction efficiency, the effect of various parameters on the efficiency of the SPME process, such as extraction time, desorption time, extraction temperature, extraction temperature and ionic strength of sample solutions, were studied. All measurements were carried out in triplicate at the level of 25 μg L^{-1} of each phenolic analyte.

3.4.1. Effect of extraction and desorption time. The extraction time is an important parameter in achieving equilibrium in the distribution of analytes between the fiber and the sample. Extraction time also determines the sensitivity and reproducibility of the proposed method. The effect of time on extraction efficiency was examined over 10–60 min with other
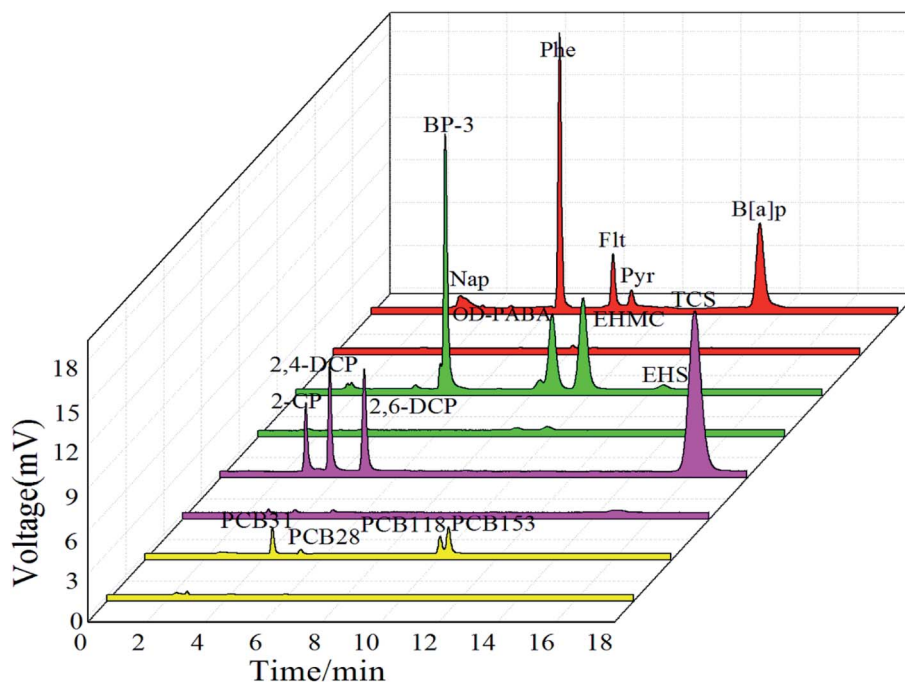
Fig. 6 Typical chromatograms from direct HPLC for PCBs (a), phenolic compounds (c), UV filters (e) and PAHs (g) in water spiked with 25 μg L^{-1}; as well as the corresponding SPME–HPLC with the PPy@TiO$_2$NPs/Ti fiber for PCBs (b), phenolic compounds (d), UV filters (f) and PAHs (h). SPME conditions: extraction time, 55 min; temperature, 40 °C; desorption time, 7 min; stirring, 300 rpm.

extraction conditions kept constant. 30 min was enough to nearly reach equilibrium between the fiber and aqueous phase (Fig. S1a†). In DI-SPME-HPLC analysis, desorption time should be optimized in order to ensure the quantitative transfer of the analytes into the HPLC injection port. After extraction, solvent desorption of the extracted phenolic compounds was performed in the mobile phase. For the target phenolic analytes, the peak area reached a constant maximum within 7 min. Consequently, extraction of 30 min and desorption of 7 min were employed in the following experiments.

3.4.2. Effect of extraction temperature. Temperature is very important for SPME because of its potential influence on mass transfer and the partitioning of target analytes between the fiber coating and sample solution.[43] Higher temperature can increase the diffusion coefficient of analytes in water and shorten the extraction time. On the other hand, temperature can decrease the partition coefficient between the coating and sample matrix because the absorption is generally an exothermic process. In addition, as the temperature rises, air bubbles tend to form in the aqueous matrix, which has adverse action on the adsorption of the analytes. Fig. S1b† presents the effect of temperature on the extraction of phenolic analytes from 20 to 70 °C. The highest extraction efficiencies were achieved at 40 °C. Subsequently, the extraction capability quickly decreased when the temperature continuously increased. Thus 40 °C was employed for further extraction.

3.4.3. Effect of stirring. Stirring is an important kinetic parameter because extraction is a dynamic diffusion-controlled process. Agitating the solution accelerates the mass transfer of the analytes from bulky solution to fiber coating, and hence

facilitates the equilibrium. The effect of sample stirring rates on the extraction efficiency in the range of 300–800 rpm was studied. The results indicated that the extraction efficiency was increased by raising the stirring rate up to 500 rpm (Fig. S1c†). The lower efficiency at higher stirring rates may be due to air bubbles formed on the fiber surface. Therefore, the optimal stirring rate was fixed at 500 rpm.

3.4.4. Effect of ionic strength. It is well known that ionic strength of the solution produces two opposite results for SPME. As shown in Fig. S1d,† a significant positive effect on the extraction efficiency of the phenolic compounds was observed in the aqueous phase with NaCl of 10% (w/v). In this case, the salt out effect played a dominant role. When the content of NaCl is greater than 10%, the extraction effect deteriorates due to the competitive adsorption of Na$^+$ and Cl$^-$. Therefore, according to the results obtained in this work, 10% NaCl was selected for all subsequent experiments.

3.5. Analytical performance of the PPy@TiO$_2$NPs/Ti fiber in the extraction of phenolic compounds

To better understand the extraction efficiency of the phenolic compounds, the PPy@TiO$_2$NPs/Ti fiber along with the fabricated fibers at different stages, were further compared with the most frequently used PA and PDMS fibers for the extraction of phenolic compounds under the same conditions. According to the results in Fig. 6, the untreated Ti wire, the TiO$_2$NPs fiber and the 100 μm PDMS fiber show negligible extraction capability for phenolic analytes except TCS (Fig. S2a–c†). The PPy@TiO$_2$NPs/Ti fiber (Fig. S2e†) presented superior extraction efficiency for all studied phenolic analytes compared to the PA fiber. This

Table 1 Analytical parameters of the proposed method with the PPy@TiO$_2$NPs/Ti fiber

Analytes	Linearity (μg L^{-1})	R^2	Recovery[a] (%)	RSD[a] (%) Single fiber ($n = 5$)	Fiber-to-fiber ($n = 3$)	LODs (μg L^{-1})	LOQs (μg L^{-1})
2-CP	0.1–200	0.9965	94.5	5.8	7.2	0.024	0.09
2,4-DCP	0.1–200	0.9982	109	4.3	5.1	0.021	0.07
2,6-DCP	0.1–200	0.9978	103	4.6	5.8	0.026	0.08
TCS	0.05–200	0.9993	107	3.5	4.6	0.008	0.03

[a] Calculated at the concentration level of 50 μg L^{-1}.

result can be attributed to the increased molecular polarity of the PPy@TiO$_2$NPs/Ti fiber surface modified by nano-PPy, which increased the extraction performance for the phenolic analytes due to the increased compatibility. At the same time, the fiber coating has higher porosity, larger specific surface area and the characteristics of TiO$_2$NPs, so the extraction effect of the fiber coating is better than that of commercial polar fiber PA. Such a PPy@TiO$_2$NPs composite coating provides a potential alternative for selective extraction of phenolic analytes from water samples.

3.5.1 Analytical performance. The analytical performance of the developed method with the PPy@TiO$_2$NPs/Ti fiber was investigated for phenolic compounds under the optimized conditions, by extracting a series of standard working solutions. Some useful analytical data including the corresponding correlation coefficients (R^2), recoveries, limits of detection (LODs), limits of quantitation (LOQs) and relative standard deviations (RSD) for the studied compounds using this fiber are listed in Table 1.

The linear calibration curves of 2-CP, 2,4-DCP and 2,6-DCP were obtained in the concentration range 0.1–200 μg L^{-1}, with the correlation coefficients (R^2) higher than 0.9965 in all instances. The linear range of TCS was 0.05–200 μg L^{-1}, and R^2 was 0.9993. The single fiber repeatability for five replicate extractions of phenolic compounds at the 50 μg L^{-1} spiked level

varied from 3.5% to 5.8%. The fiber-to-fiber reproducibility for three parallel PPy@TiO$_2$NPs/Ti fibers fabricated in different batches ranged from 4.6% to 7.2%. The LODs and LOQs ranged from 0.008 to 0.026 μg L^{-1} and from 0.03 to 0.09 μg L^{-1} for phenolic compounds based on the signal to noise ratio (S/N) of 3 and 10, respectively.

3.5.2. Analysis of real water samples. To evaluate the reliability of the proposed method, the presented DI-SPME-HPLC-UV method using the PPy@TiO$_2$NPs/Ti nanocomposite coated fiber was applied to the preconcentration and determination of target chlorophenols and triclosan in river water, wastewater and tap water. The analytical results are summarized in Table 2. No phenolic compounds were found in tap water, but they were detected in the Yellow River water (except 2-CP) and wastewater, especially TCS. The reason is that TCs is an effective external antibacterial disinfectant, which is widely used in high efficiency soaps, sanitary lotion, underarm deodorant, air freshener, refrigerator deodorant, *etc.*, which increase the content of it in environmental water accordingly. To evaluate the matrix effect, water samples were spiked with standards of target phenolic compounds at concentrations of 5.0 and 10 μg L^{-1}, respectively. As can be seen in Table 2, relative recoveries were between 89.7% and 112%, and RSDs varied from 3.49% to 7.24%. Fig. S3† shows typical chromatograms of direct HPLC and SPME-HPLC for phenolic compounds in wastewater. The

Table 2 Analytical results of phenolic compounds in different environmental water samples

Water samples	Analyte	Original (μg L^{-1})	Spiked with 5 μg L^{-1} Detected (μg L^{-1})	Recovery (%)	RSD (%)	Spiked with 10 μg L^{-1} Detected (μg L^{-1})	Recovery (%)	RSD (%)
Yellow River	2-CP	ND[a]	4.73	94.6	5.15	9.88	98.8	6.73
	2,4-DCP	0.142	5.08	98.8	4.53	9.72	95.8	5.84
	2,6-DCP	0.113	5.32	104	4.37	11.1	110	5.36
	TCS	3.52	9.17	108	3.49	14.2	105	4.91
Wastewater	2-CP	0.771	6.12	106	5.34	11.2	104	6.62
	2,4-DCP	2.26	6.51	89.7	4.68	11.3	92.3	5.39
	2,6-DCP	0.762	6.45	112	4.72	11.3	105	5.75
	TCS	1.43	6.58	103	4.13	12.5	109	5.03
Tap water	2-CP	ND	4.72	90	6.03	9.67	96.7	7.24
	2,4-DCP	ND	5.44	108	4.71	10.7	107	5.35
	2,6-DCP	ND	5.23	104	4.82	10.3	103	5.68
	TCS	ND	5.30	106	4.07	10.7	107	5.22

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

PPy@TiO$_2$NPs/Ti fiber exhibits a much enhanced extraction efficiency for target analytes. These data demonstrate the applicability of the developed method for the analysis of trace phenolic compounds in environmental water samples.

3.6. Stability of the PPy@TiO$_2$NPs/Ti fiber

The stability of the metal-based fibers greatly depends on their coating procedures, coating structures and surface properties.[44] In our study, the PPy@TiO$_2$NPs coating was modified on the surface of TiO$_2$NPs grown *in situ* on a Ti fiber substrate with characteristics of good mechanical properties, easy acquirability, flexibility and robustness. The fabricated fiber was immersed in 0.01 mol L^{-1} NaOH and 0.01 mol L^{-1} H$_2$SO$_4$ for 12 h, respectively. As a matter of fact, negligible morphological changes were observed from its SEM image. In order to examine its reusability, the PPy@TiO$_2$NPs/Ti fiber was soaked in buffer solution and methanol for 15 minutes in sequence to imitate the extraction process in the SPME procedure. The obtained results revealed that the fabricated fiber could be used at least 250 times for extraction and desorption of phenolic compounds. In this case, the acceptable average recovery (85.2–93.5%) and RSDs (4.23–7.34%) were still achieved for five replicate analyses of the target phenolic compounds at the level of 50 μg L^{-1}. However, what matters is that highly concentrated anionic species might reduce the lifetime of the coating due to the changes in the structure or morphology of the polymer during an exchange of counter ions.[45]

4. Conclusion

In this study, a new PPy@TiO$_2$NPs/Ti fiber was prepared by the electropolymerization of PPy on the surface of annealed TiO$_2$-NPs. The proposed fiber coating has many advantages, such as a porous structure, it is inexpensive and easy to prepare, has a long lifespan, strong interactions, reproducible preparation, and strong adhesion to the Ti matrix. Application of the novel nanocomposite coating as an adsorbent material in direct immersion solid phase microextraction of chlorophenols and triclosan was investigated. The results demonstrated that the fiber exhibits excellent extraction efficiency and good selectivity for SPME of phenolic compounds due to its unique surface properties and larger available surface area. The extraction performance of the PPy@TiO$_2$NPs coating for the selected phenolic compounds is superior to that of commercial PA fiber because it had a higher affinity for the studied phenolic compounds.

Conflicts of interest

There are no conflicts to declare.

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