Electronic supplementary material

Development of a novel porous cobalt, phosphorus and nitrogen co-doped carbonaceous coating by phosphiding ZIF-67 grown on Nitinol fiber for selective solid-phase microextraction of polycyclic aromatic hydrocarbons from water samples

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Experimental Section

Electrodeposition of the Co coating

The bare NiTi wires (55 mm in length) were ultrasonically cleaned with acetone and ultra-pure water for 10 min, respectively. Then, the bare NiTi wires were activated in a solution of HF, HNO_3 and H_2O (1/4/5, v/v/v) for 2 min. After ultrasonic cleaning in ultra-pure water, the pretreated NiTi wires were dipped into the electrolytic solution as a working electrode, the Pt rod as a counter electrode and the saturated calomel electrode (SCE) as a reference electrode

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in the three-electrode system. $Co(Ac)_2$ solution of 0.1 $mol \cdot L^{-1}$ served as an electrolyte, and –1.1 V was applied to the system at 40 °C for 1000 s. The NiTi wire with the Co coating (NiTi@Co) was thoroughly rinsed for subsequent in situ growth of ZIF-67.

Electrochemical in-situ growth of the ZIF-67 coating

Typically, 0.8 g of 2-MIM was dissolved in the solution of 7.5 mL DMF and 2.5 mL ultra-pure water as an electrolyte. The NiTi@Co fiber was dipped into the electrolyte as a working electrode, the Pt rod as a counter electrode and the SCE as a reference electrode in the three-electrode system. 4 V was applied to the system at 60 °C for 700 s. The resulting fiber was washed with methanol several times, and then dried in an oven at 80 °C to obtain the NiTi@Co@ZIF-67 fiber.

Fabrication of the Co-P-NC coatings

Firstly, the NiTi@Co@ZIF-67 fiber was placed in a porcelain boat, and 3 g of NaH_2PO_2 was placed in the other one located at upstream side in a tubular furnace. Then, the temperature increased from room temperature to 300 °C with a ramping rate of 2 $°C \cdot min^{-1}$ holding for 2 h in N_2 atmosphere. Phosphorus was introduced into the N-doped carbonaceous coating derived from ZIF-67 grown on the NiTi substrate at the same time by the reaction of ZIF-67 with NaH_2PO_2. Thereafter, the fabricated fiber was cooled to room temperature. Finally the fabricated fiber was mounted to the SPME holder and conditioned in the SPME-LC interface for 30 min prior to use.

Optimization of SPME conditions for PAHs

The detailed optimal results were shown in Fig. S1. As shown in Fig. S1a, pH has a little effect

on the adsorption efficiency. In this study, NaCl of 15–35% (w/v) was investigated. As shown in Fig. S1b, the adsorption efficiency was gradually increased with the increasing content of NaCl from 15% to 30%, and thereafter decreased at higher content of NaCl. In the following experiments, NaCl of 30% was selected to maintain the ionic strength of aqueous solution.

Stirring is an essential process to improve mass transfer and reduce the equilibration time. Therefore, stirring rate was studied over the range of 400-800 rpm. As shown in Fig. S1c, the highest adsorption efficiency was obtained at the stirring rate of 600 rpm. Furthermore, adsorption temperature also facilitates the diffusion of PAHs from the sample solution into the fiber coating. Nevertheless, higher adsorption temperature would adversely affect the adsorption performance due to the exothermic adsorption and the increased solubility of PAHs in water phase. As shown in Fig. S1d, the highest adsorption efficiency was achieved at the critical temperature of 35 °C. Therefore, 35 °C was selected for subsequent experiments. In addition, adsorption and desorption time are important factors in SPME. As can be seen in Fig. S1e and Fig. S1f, the adsorption equilibria were reached within 35 min, and the desorption equilibria of PAHs was achieved in the mobile phase within 4 min. Therefore, 35 min was selected for adsorption and 4 min were selected for desorption in subsequent study.

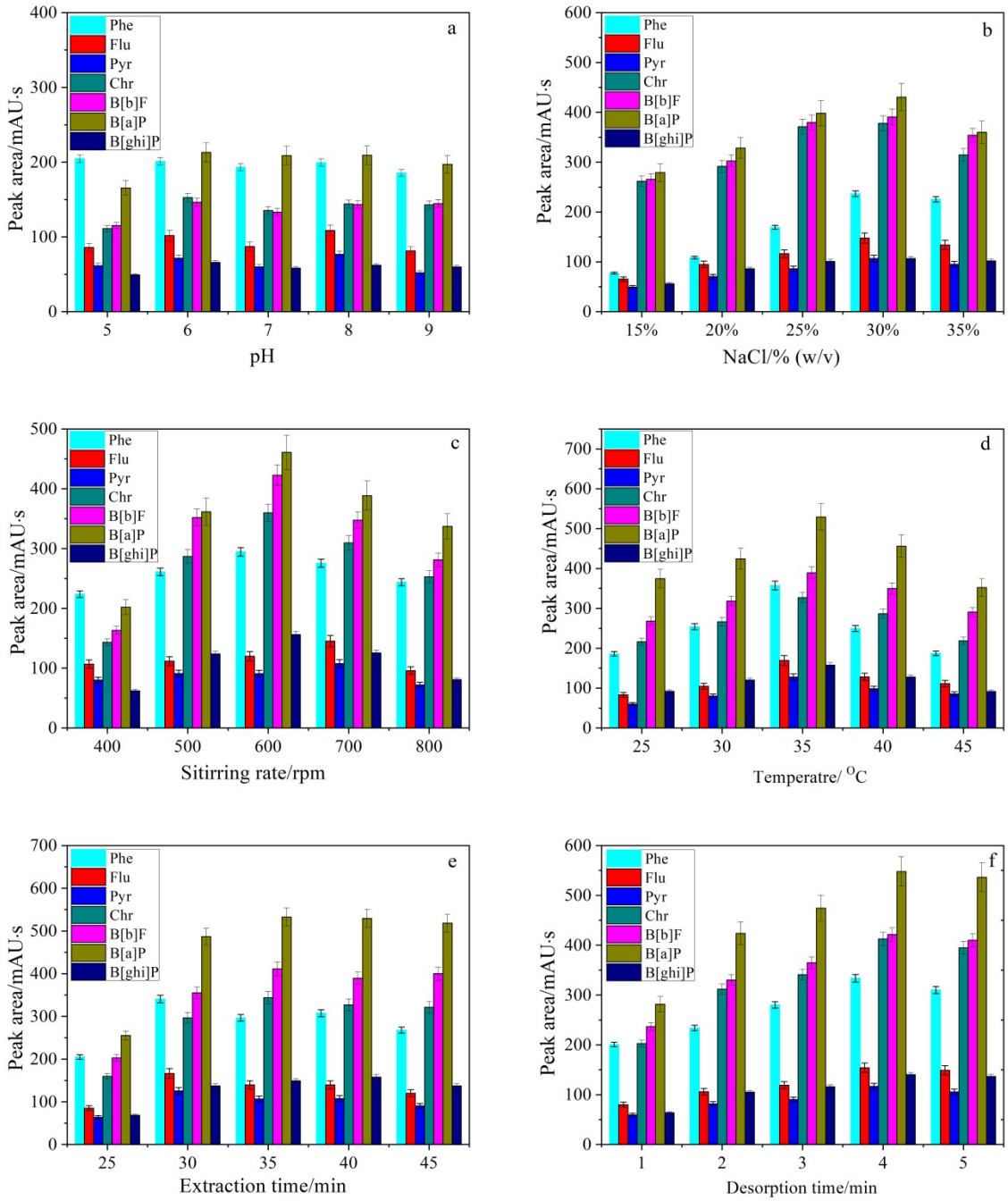

Fig. S1 Effect of pH (a), ionic strength (b), stirring rate (c), extraction temperature (d), extraction time (e) and desorption time (f) on the extraction efficiency.

Table S1 Analytical results for the enrichment and determination of target PAHs in real water samples (n = 3)

Samples	Analytes	Original ($\mu g \cdot L^{-1}$)	Spiked (5.0 $\mu g \cdot L^{-1}$)			Spiked (10 $\mu g \cdot L^{-1}$)		
			Found ($\mu g \cdot L^{-1}$)	Recovery (%)	RSDs (%)	Found ($\mu g \cdot L^{-1}$)	Recovery (%)	RSDs (%)
Snow water	Phe	0.73	5.05	86.4	5.30	10.69	99.6	5.18
	Flu	ND	4.68	93.6	6.51	9.14	91.4	6.16
	Pyr	ND	4.99	99.7	6.84	10.10	101	5.08
	Chr	ND	4.61	92.1	5.47	8.54	85.4	6.62
	B[b]f	0.12	4.57	88.9	4.25	10.82	107	5.63
	B[a]p	0.69	5.74	101	5.83	10.42	97.3	5.49
	B[ghi]p	ND	5.10	102	6.82	9.76	97.6	4.50
Wastewater	Phe	0.39	4.73	86.7	7.56	8.51	81.2	7.04
	Flu	0.62	4.99	87.4	8.68	9.00	83.8	6.32
	Pyr	0.58	5.27	93.8	7.79	8.46	78.8	7.86
	Chr	0.87	4.85	79.6	6.10	8.86	79.9	8.42
	B[b]f	1.10	4.92	76.3	8.51	10.5	93.6	5.88
	B[a]p	0.62	4.98	87.1	8.81	9.94	93.2	6.72
	B[ghi]p	ND	3.73	74.5	6.96	8.85	88.5	5.10
River water (Site 1 in upper section)	Phe	1.65	6.27	92.4	5.77	11.75	101	4.82
	Flu	ND	4.95	99.0	4.29	9.67	96.7	5.56
	Pyr	ND	5.15	103	5.66	9.48	94.8	5.48
	Chr	ND	4.73	94.6	5.23	10.3	103	7.73
	B[b]f	ND	5.25	105	6.79	9.83	98.3	6.22
	B[a]p	0.42	5.09	93.3	5.30	10.5	101	5.09
	B[ghi]p	ND	4.60	91.9	5.63	9.66	96.6	5.67
River water (Site 2 in suburb)	Phe	1.29	6.18	97.8	6.36	11.07	97.8	5.55
	Flu	0.62	5.46	96.7	5.51	10.72	101	5.37
	Pyr	0.93	5.70	95.3	5.89	10.65	97.2	6.02
	Chr	ND	5.10	102	5.67	10.40	104	5.29
	B[b]f	ND	5.05	101	5.79	9.34	93.4	5.21
	B[a]p	0.51	5.47	99.1	6.75	10.61	101	7.06
	B[ghi]p	ND	4.58	91.5	5.04	9.04	90.4	5.89
River water (Site 3 in urban)	Phe	0.23	5.43	104	6.26	9.7	94.7	5.77
	Flu	ND	4.59	91.8	6.03	9.85	98.5	7.58

Pyr	0.58	5.46	97.6	7.52	10.2	96.4	6.75
Chr	0.21	4.96	95.0	7.44	10.5	103	5.13
B[b]f	ND	4.82	96.4	6.13	9.38	93.8	5.86
B[a]p	0.70	5.8	102	5.35	9.92	92.2	6.02
B[ghi]p	ND	4.565	91.3	4.23	10.1	101	4.64

[a] ND, not detected or lower than LOD