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Supplementary information

Application of ordered mesoporous carbon in solid phase microextraction for fast mass transfer and high sensitivity

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1. Experiments

1.1 Chemicals and reagents

The triblock copolymer F127, phenol (99.0%), benzene (99.9%), *m*-xylene (99.5%), toluene (99.8%) and ethylbenzene (99.8%) were bought from Aladdin (Shanghai, China). The ethanol (A.R.), cyclohexane (A.R.), tetraethyl orthosilicate (TEOS, A.R.), sodium hydroxide (NaOH, A.R.), formaldehyde (w/v, 37%), hydrochloric acid (HCl, A.R.) were obtained from Guangzhou

Chemical Reagent Factory (Guangzhou, China). Neutral silicone sealant was bought from Sikasil Ltd (Guangzhou, China). Naphthalene, acenaphthene and pyrene were purchased from Sigma-Aldrich (Shanghai, China). The Sylgard 184 silicone elastomer base was purchased from Dow Corning (Shenzhen, China).

The commercial polydimethylsiloxane (PDMS) fibers (30/100 μm) were purchased from Supelco (Bellefonte, PA, USA) and the stainless steel wires were bought from Small Parts (Miami, FL, USA).

1.2 Characterizations

The surface morphology of prepared OMC-coated fiber was observed through scanning electron microscopy (SEM) on a Quanta 400F (FEI/OXFORD/HKL, Dutch). In addition, the transmission electron microscope (TEM, FEI Tecnai G2 Spirit, FEI/OXFORD/HKL, Dutch) and X-Ray Diffractometer (XRD, SmartLab, Rigaku, Japan) were employed to characterize the synthesized OMC. Nitrogen adsorption-desorption isotherms at 77 K were measured with a Micromeritics ASAP 2020 analyzer. The Brunauer-Emmett-Teller (BET) method and Barrett-Johner-Halendar (BJH) method were adopted to analyze the surface areas and pore size distributions, respectively. The SPME procedures were carried out with gas chromatography-mass spectrometry (GC-MS, 6890-5975) and gas chromatography-flame ionization detector (GC-FID, 7890A).

1.3 Synthesis of OMC

OMC was prepared by a EISA method.[1] Typically, 1.3 mL of 5 M NaOH solution and 10.4 g of formaldehyde (37 wt%) were added to 6.1 g melt phenol. After stirred for 0.5 h at 70 °C, the mixed solution was cooled to room temperature and the pH value was adjusted to about 7.0 by 5 M HCl solution. The resol precursor was prepared by diluting the mixed solution using ethanol until the solution volume was 100 mL. Subsequently, 1.6 g of block copolymer F127 was dissolved in 8 g of ethanol with 1 mL of 0.2 M HCl solution. Then, 2 mL of TEOS and 10 mL of the prepared resol precursor solution were added into the F127 solution. The reaction solution was transferred to the dish after stirred for 2 h. After volatilizing ethanol at room temperature for 12 h, the thermopolymerization reaction was conducted at 100 °C and kept for 24 h in an oven. The as-made products were scraped from the dishes and calcined in a tubular furnace to obtain the carbon-silica nanocomposite. The calcination procedure in N_2 flow was as follows: The temperature was increased from 50 to 600 °C at the heating rate of 1 $°C\cdot min^{-1}$; next, the temperature was raised to 900 °C at 5$°C\cdot min^{-1}$ and kept for 2 h at 900 °C. After immersed in 10 wt% HF solution for 24 h, the silica was removed from the carbon-silica nanocomposite to obtain OMC.

1.4 Preparations of the OMC-coated fibers

The stainless steel wires were cut into 3 cm and cleaned by ultrapure water, acetone and ultrapure water in turn. Next, the cleaned stainless steel wires were inserted into the diluted neutral silicone sealant solution, which was obtained by sonicating the mixture of 0.5 g neutral silicone sealant and 1 mL cyclohexane for 10 min. After pulling the stainless steel wire from the neutral silicone sealant solution, the stainless steel wire was coated with a thin layer of OMC powder. The coating procedure was repeated for three times in order to get appropriate thickness. Finally, the prepared fibers were treated at 250 °C and 350 °C for 1 h in N_2 flow, respectively, for removing the adsorbed substances and residual solvents prior to use.

1.5 SPME procedure

All SPME experiments were performed at the mode of headspace in aqueous and nonaqueous samples. The aqueous sample was prepared by adding 10 mL ultrapure water mixed with PAHs and BTEX standard samples into 20 mL glass vial. On the other hand, the mixture of 5 g Sylgard 184 silicone elastomer base and 50 mg naphthalene/ acenaphthene were placed into 20 mL glass vial to prepare nonaqueous sample. The nonaqueous sample for PDMS-coated fiber was prepared by mixing 5 g SYLGARD 184 silicone elastomer base with 500 μL benzene (sample 1), while that for OMC-coated fiber was prepared by mixing 5 g SYLGARD 184 silicone elastomer base with 5 μL benzene (sample 2). The prepared OMC-coated fiber was inserted into the vial contained the analytes and the fiber coating was exposed to headspace for extraction. After extraction, the fiber was withdrawn and inserted into the injection of GC-MS/FID for thermal desorption at 250 °C.

2. Investigation of Adsorption Theory

Adsorption isotherms. The adsorption isotherm indicates how the adsorption molecules distribute between the gas phase and the solid phase when the adsorption process reaches an equilibrium state. It is important to find the suitable model that can be used for fitting the isotherm data to different isotherm models. The Langmuir and Freundlich models are the most common used according to the reported models. The relationship between the extraction amount of benzene, naphthalene and acenaphthene and the OMC was described by Langmuir and Freundlich models in this study. The Langmuir isotherm equation is represented by the following equation:

$$Q = \frac{K_L C}{1 + aC}$$

C is equilibrium concentration (μg·L^{-1}) and Q is equilibrium amount of analyte per unit weigh of adsorbent (μg·g^{-1}); K_L and α are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and energy of adsorption.

The Freundlich isotherm is represented by the following exponential form:

$$Q = K_F C^{1/n}$$

K_F and n are Freundlich constants, n indicates how favorable the adsorption process is and K_F is the adsorption capacity of the adsorbent.

Adsorption Kinetics. Two kinds of kinetic models are tested to fit the data obtained from the experiments in order to elucidate the adsorption mechanism. The pseudo-first-order equation is a simple kinetic model that describes the process of adsorption:

$$\frac{dq_t}{dt} = k_1(q_{e,1} - q_t) \qquad (1)$$

where k_1 (min^{-1}) is the rate constant of the adsorption, $q_{e,1}$ and q_t refer to the analytes adsorbed (μg·g^{-1}) at equilibrium and at any time, t (min) .

Kinetic data are further treated with the pseudo-second-order kinetic model:

$$\frac{dq_t}{dt} = k_2(q_{e,2} - q_t)^2 \tag{2}$$

where k_2 (g·μg^{-1}·min^{-1}) is the rate constant of pseudo-second-order.

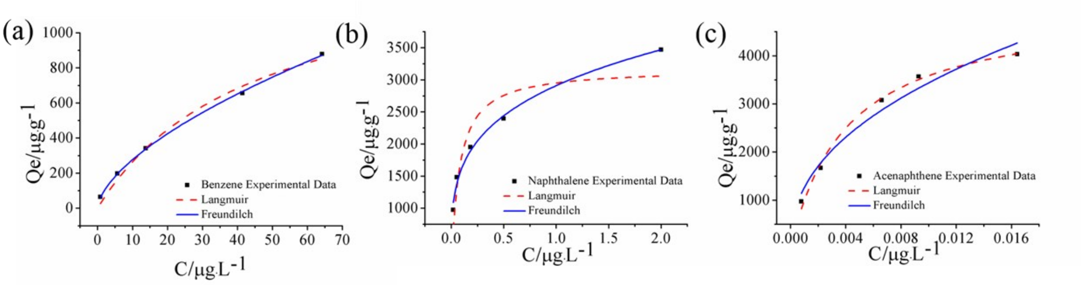

Fig. S1. The experimental data of benzene (a), naphthalene (b) and acenaphthene (c) fitted to the Langmuir and Freundlich models.

Table S1. The Langmuir and Freundlich parameters and the correlation coefficients calculated from experimental data.

Compounds	Langmuir			Freundlich		
	K_L	a	R_L	K_F	n	R_F
Benzene	32.36	0.02237	0.9857	66.77	1.6	0.9995
Naphthalene	41833	13.18	0.8161	2909	3.9	0.9900
Acenaphthene	1.2E6	244.7	0.9926	25466	2.3	0.9614

* K_L and α are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and energy of adsorption. K_F and n are Freundlich constants; n indicates how favorable the adsorption process is and K_F is the adsorption capacity of the adsorbent. R_L and R_F are correlation

coefficients of the fitted equations.

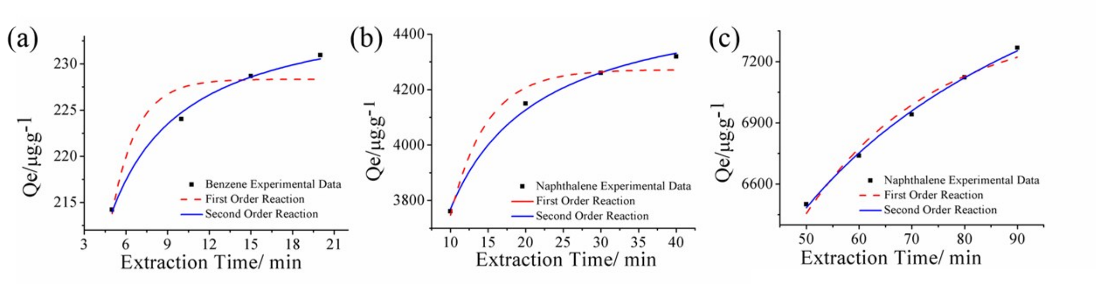

Fig. S2. The experimental data of benzene (a), naphthalene (b) and acenaphthene (c) fitted to the pseudo-first-order and pseudo-second-order models.

Table S2. The pseudo-first-order and pseudo-second-order parameters and the correlation coefficients calculated from experimental data.

Compounds	Experimental	pseudo-first-order			pseudo-second-order		
	q_e (μg·g^{-1})	K_1	$q_{e,1}$	R_1	K_2	$q_{e,2}$	R_2
Benzene	231.3	0.55	228.3	0.8305	0.53	236.7	0.9932
Naphthalene	4553	0.012	4272	0.9539	2.1	4559	1.000
Acenaphthene	7293	0.041	7405	0.9721	60	7277	0.9964

* k_1 and k_2 are the rate constants of the adsorption, $q_{e,1}$ and $q_{e,2}$ refer to the analytes adsorbed at equilibrium.

3. Optimizations of SPME parameters

Extraction temperature. For headspace SPME, increasing extraction temperature can enhance the mass transfer, but decrease the partition coefficient of analytes between OMC-coated fiber and sample solution. Extraction temperature profiles of BTEX are shown in Fig. S1a and for three PAHs are shown in Fig. S2a. Then, the extraction temperature of 30 °C for BTEX was chosen for the following experiments, while 60 °C was suitable for the extraction of PAHs.

Extraction time. Since SPME is an equilibrium-based technique, it is important to select optimum extraction time for the method development. The influence of extraction time for BTEX was determined from 1 to 12 min and the equilibrium time of 7 min was shown in Fig. S1b. The extraction time curves for PAHs were investigated ranging from 20 to 60 min. The peak areas of three PAHs were increasing until the extraction time was 40 min (Fig. S2b), thus, 40 min was selected as the optimal extraction time for PAHs.

Desorption temperature and desorption time. Higher desorption temperature and longer desorption time can make the analytes desorb thoroughly from the OMC coating, but may shorten the coating life span. Hence, it is necessary for desorption temperature and time to be optimized. According to the optimization results of BTEX (Figs. S1c and S1d), the desorption temperature of 300 °C and desorption time of 4 min were chosen, while the desorption temperature of 325 °C and desorption time of 3 min were selected for the following desorption procedure for PAHs (Figs. S2c and S2d).

Salt concentration. The influence of salt concentration on extraction efficiency was investigated by varying the NaCl concentration from 0 to 10% (w/v). The ionic strength of the sample solution increases and the phenomenon of salting out occurs as the NaCl concentrations increase, resulting in higher extraction efficiency. From the results, concentration of NaCl in BTEX working solutions was fixed 5% in all extraction process (Fig. S1e) and the concentration of 10% was applicable for PAHs (Fig. S2e).

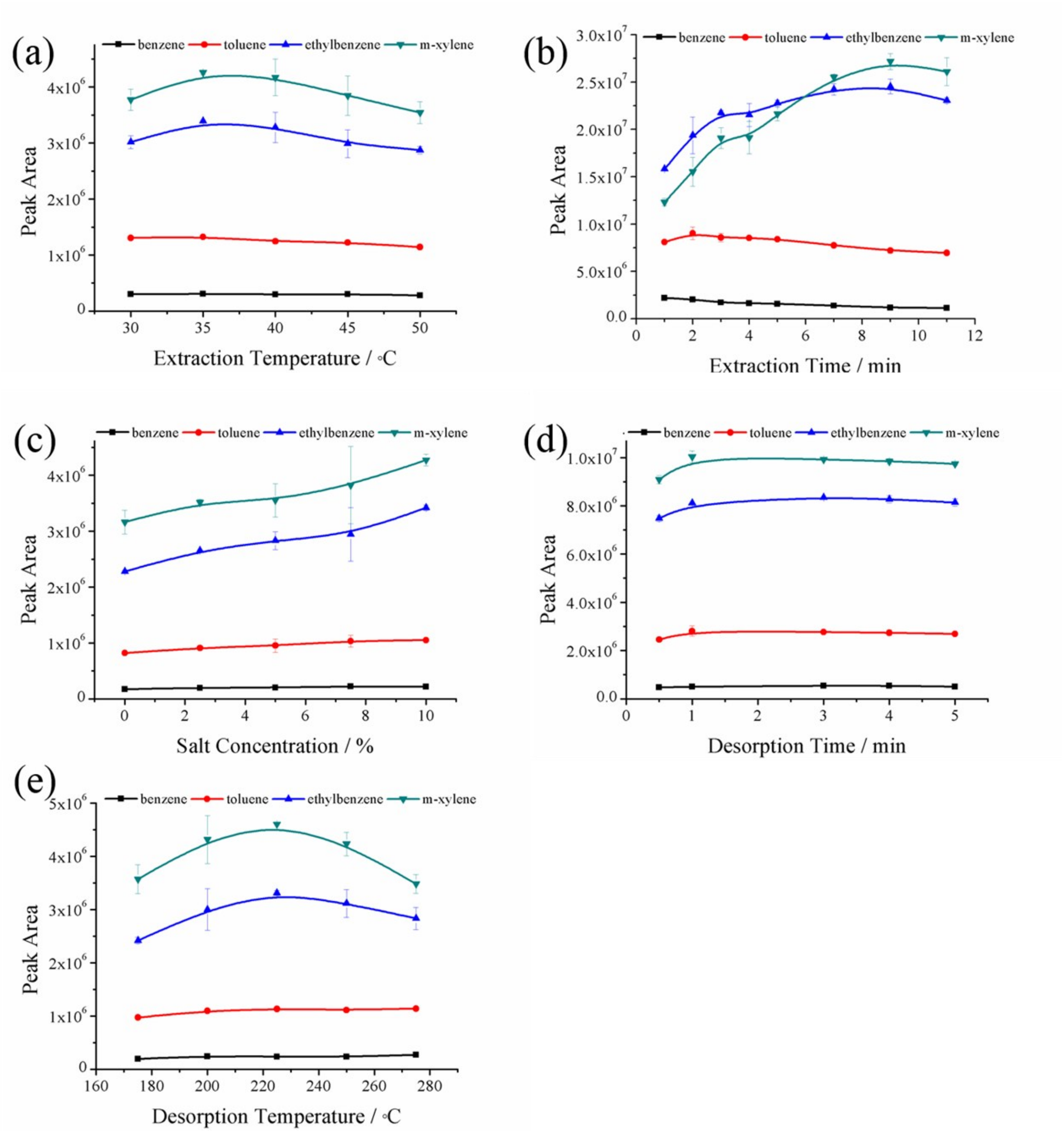

Fig. S3. Optimization of SPME parameters for BTEX by employing the OMC-coated fiber. (a) Extraction temperature; (b) extraction time; (c) salt concentration; (d) desorption time; (e) desorption temperature.

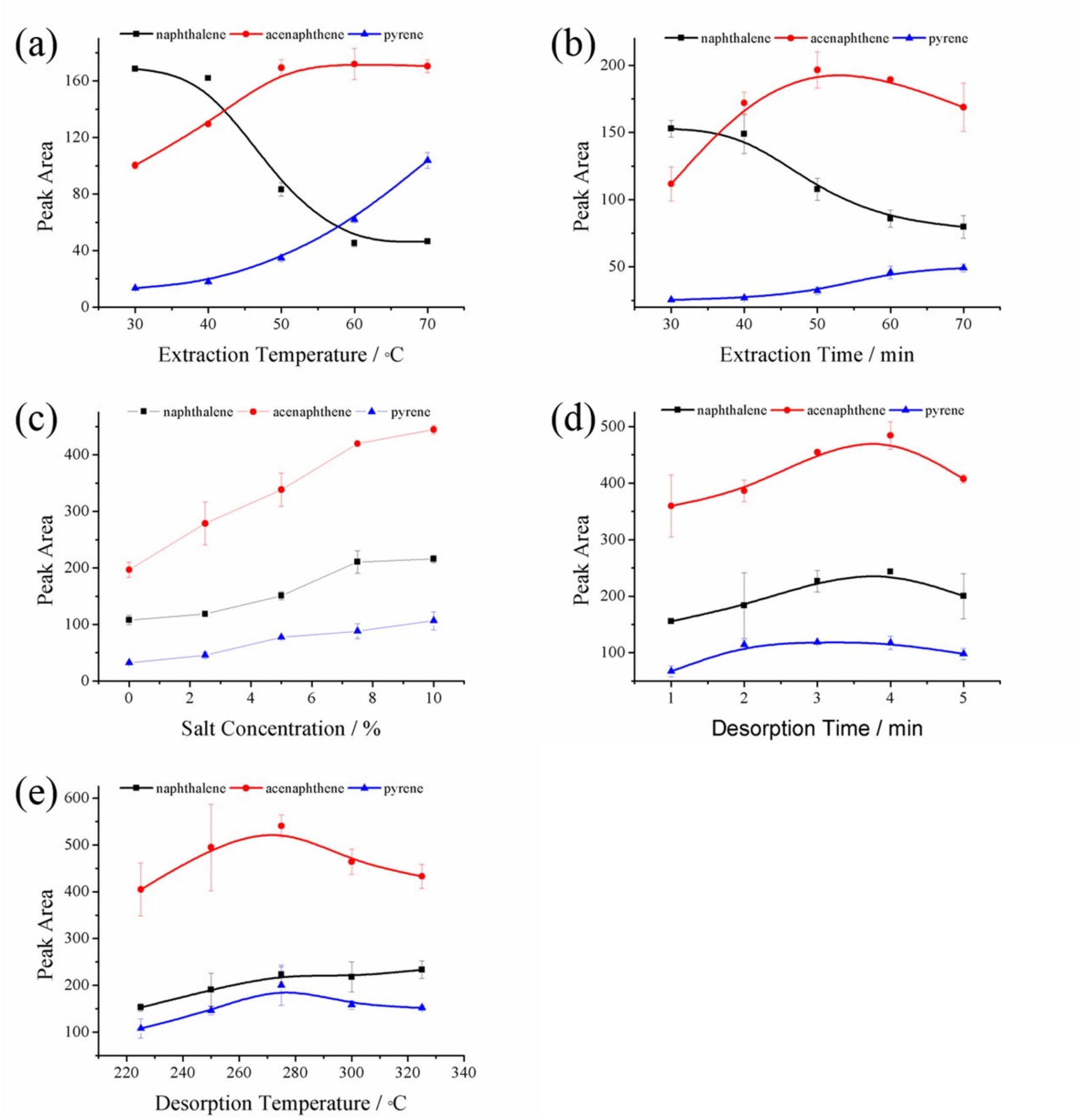

Fig. S4. Optimization of SPME parameters for PAHs by employing the OMC-coated fiber. (a) Extraction temperature; (b) extraction time; (c) salt concentration; (d) desorption time; (e) desorption temperature.

4. Thermostability of the OMC-coated fiber

As adsorbents of SPME fiber coating, it is necessary to investigate the thermostability because of the requirements of high temperature for thermal desorption. Efforts were then made to elucidate the thermostability of the OMC-coated fiber by conditioning the fiber at 250, 270, 290, 310, 330 and 350 °C for 1h before extraction. The extraction curves (Fig. S5) for BTEX increased as the heat-treatment temperature became higher and the curves for PAHs always kept stable, which illustrated that the OMC was heat resisting. Higher condition temperatures were helpful to desorb the non-targeted substances from the OMC completely, leading to larger extraction amounts for target analytes.

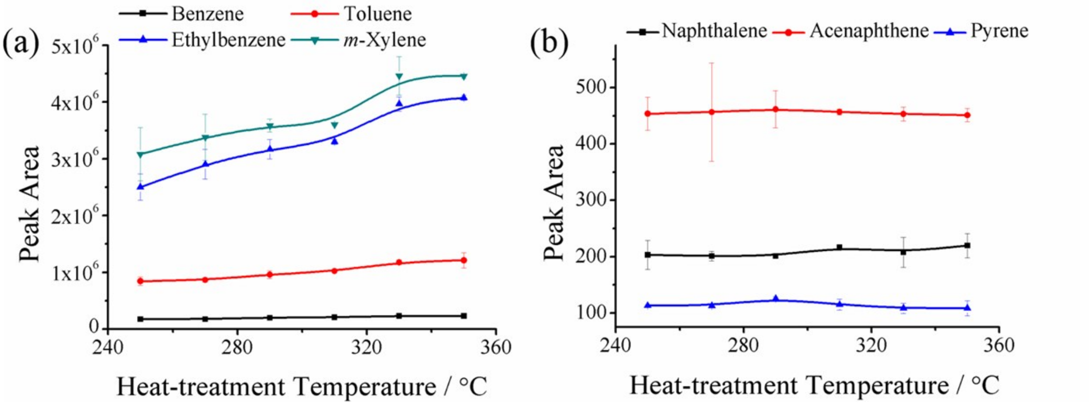

Fig. S5. Extraction efficiencies towards BTEX (a) and PAHs (b) after the OMC-coated fiber was treated under different temperatures.

5. Analytical performance of the OMC-coated fiber

Table S3 Analytical performance of the OMC-coated fiber.

Compound	Linear Range($ng\cdot L^{-1}$)	Correlation Coefficient (R)	LODs ($ng\cdot L^{-1}$)	Single fiber (n=6, RSD %)	Fiber-to-fiber (n=3, RSD %)
Benzene	5-2000	0.9990	0.14	4.1	8.9
Toluene	5-2000	0.9996	0.26	2.7	7.3
Ethylbenzene	5-2000	0.9999	0.01	3.7	6.2
m-Xylene	5-2000	0.9999	0.02	3.4	6.1
Naphthalene	10-2000	0.9996	0.27	5.3	4.0
Acenaphthene	5-2000	0.9999	0.08	4.4	4.0
Pyrene	50-2000	0.9993	8.5	6.0	4.6

Table S4. The comparison of LODs between the OMC-coated fiber and the reported works.

Compounds	LODs ($ng\cdot L^{-1}$)					
	OMC-coated fiber	Ref.2	Ref.3	Ref.4[a]	Ref.5	Ref.6
Benzene	0.14	5.4	0.01×10^3	0.3×10^3	-	-
Toluene	0.26	5.5	0.005×10^3	-	-	-
Ethylbenzene	0.01	3.2	0.005×10^3	0.9×10^3	-	-
m-Xylene	0.02	6.6	0.001×10^3	-	-	-
Naphthalene	0.27	3.9	-	-	2.70	0.24×10^3
Acenaphthene	0.08	0.3	-	-	1.64	0.26×10^3
Pyrene	8.5	2.2	-	-	2.32	0.63×10^3

Note: The unit of LODs in Refs.3, 4 and 6 was $\mu g\cdot L^{-1}$ and converted to $ng\cdot L^{-1}$

Table S5. The comparison of LODs between the OMC-coated fiber and the reported works based on carbon materials.

Compounds	LODs ($ng \cdot L^{-1}$)					
	OMC-coated fiber	Ref.7	Ref.8	Ref.9	Ref.10	Ref.11
Benzene	0.14	3	0.047×10^3	0.02×10^3	-	-
Toluene	0.26	2	0.0026×10^3	0.015×10^3	-	-
Ethylbenzene	0.01	0.7	0.008×10^3	0.005×10^3	-	-
m-Xylene	0.02	-	-	-	-	-
Naphthalene	0.27	-	-	-	5	1.5
Acenaphthene	0.08	-	-	-	20	1.2
Pyrene	8.5	-	-	-	-	1.6

Note: The unit of LODs in Refs. 8 and 9 was $\mu g \cdot L^{-1}$ and converted to $ng \cdot L^{-1}$.

Table S6 Analytical results for the determinations of BTEX and PAHs in the Pearl River water and pond water samples.

Compound	Pearl River water sample			Pond water sample		
	Origin Concentrations ($ng \cdot L^{-1}$)	Spiked Concentrations ($ng \cdot L^{-1}$)	Recoveries	Origin Concentrations ($ng \cdot L^{-1}$)	Spiked Concentrations ($ng \cdot L^{-1}$)	Recoveries
Benzene	nd	200	95.7	nd	150	117
Toluene	nd	200	94.3	nd	150	95.0
Ethylbenzene	nd	200	96.2	nd	150	108
m-Xylene	199	200	95.1	nd	150	116
Naphthalene	44.8	50.0	102	38.4	50.0	113
Acenaphthene	8.74	15.0	97.1	nd	50.0	110
Pyrene	784	800	94.9	640	600	115

Note: nd stands for not detected.

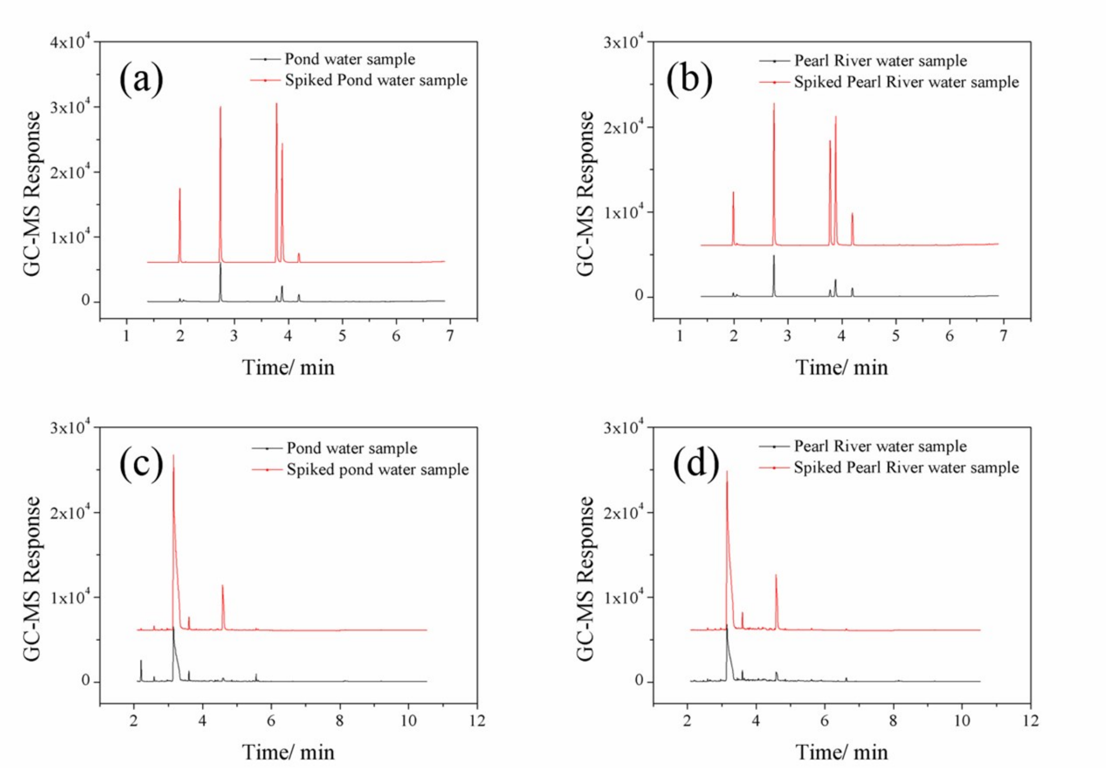

Fig. S6. Chromatograms of BTEX from pond water (a), BTEX from Pearl River water sample (b), PAHs from pond water (c) and PAHs from Pearl River water sample (d).

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