

Supplementary Information

Electrophoretic deposition of ordered mesoporous carbon nitride on a stainless steel wire as a high-performance solid phase microextraction coating

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Experiments

Chemicals and reagents:

Tetraethyl orthosilicate, ethylenediamine (EDA), carbon tetrachloride (CTC), and triblock copolymer poly (ethyleneglycol)-block-poly (propylene glycol)-block poly (ethylene glycol) (Pluronic P123, molecular weight 5800, EO20PO70EO20) were obtained from Aldrich (St. Louis, MO, USA). Melamine (2, 4, 6-Triamino-1, 3, 5-triazine) and sodium chloride were purchased from Merck (Darmstadt, Germany). The polycyclic aromatic hydrocarbons (PAHs) including naphthalene (Nap), acenaphthylene (AcPy), flurene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt) and pyrene (Pyr) were obtained from Sigma-Aldrich. Undecane, dodecane, undecanol and dodecanol were purchased from Sigma-Aldrich. Additionally, all the organic solvents such as methanol and acetone were of HPLC grade and obtained from Sigma-Aldrich. Standard solutions were prepared by appropriate dilution of the stock solution in methanol. Stock and working standards were stored at 4 °C in the refrigerator.

Apparatus

Analysis of the model compounds was performed with an Agilent 7890A GC system (Agilent Technologies, Palo Alto, CA, USA) with a FID detector and 7890B GC with a 5977B MS equipped with a split/splitless injector. The injector was used in the splitless mode at 300 °C. The column used for the separation with GC-FID was a Varian wall coated fused silica capillary column (30 m 0.32 mm, i.d., film thickness 0.25 µm). The FID temperature was fixed at 300 °C. Ultrapure helium and nitrogen (>99.999%) were used as the carrier and makeup gas at 2 mL min⁻¹ and 25 mL min⁻¹, respectively.

GC-MS separations was performed using a HP-5MS capillary column with a length of (30 m × 0.25mm) with a film thickness of 0.25 μm. The mass spectrometer was operated in the electron impact ionization mode with an ionizing energy of 70 eV. The interface and ion source temperatures were both set at 300 °C.

Separation of PAHs, alkanes and alcohols was achieved using temperature programs as follows: the oven temperature was initially held at 60 °C for 1 min and programmed at 7 °C min⁻¹ to 180 °C; at 10 °C min⁻¹ to 280 °C; held for 5 min. Helium (99.999%) was used as the carrier gas at a flow rate of 1 mL min⁻¹.

Characterizations:

The morphology of MCN and g-CN was observed with scanning electron microscopy (FE-SEM) MIRA3TESCAN-XMU (Czech Republic). Transmission electron microscope (TEM) was observed on a JEOL Ltd. JEM-2100 spectrometer. XRD patterns were recorded on a Rigaku diffractometer using Cu Ka ($\lambda = 0.154$ nm). Radiation in the 2θ ranges from 0.8 to 10° with a 2θ step size of 0.01° and a step time of 1 s. The Brunauer-Emmett-Teller specific surface areas and BJH of typical products were measured at 77 °K using an ASAP 2020 porosimeter from (Micromeritics Instrument Corp., USA).

Synthesis of g-CN:

g-CN was prepared by directly heating melamine in the semi-closed system to prevent sublimation of melamine^{1,2}. 10 g of melamine powder was put into an alumina crucible with a cover, then heated to 550 °C in a muffle furnace for 2 h at a heating rate of 20 °C min⁻¹.

Synthesis of MCN:

The synthesis of SBA-15 using the poly(ethyleneglycol)-block-poly(propylene glycol)-blockpoly(ethylene glycol) (EO₂₀PO₇₀EO₂₀, average molecular weight 5800, Aldrich) amphiphilic triblock copolymer was carried out using the procedure reported by Vinu et al³. The synthesis was performed as illustrated below: 4 g of the amphiphilic triblock copolymer was dispersed in water (30 g) and HCl solution (120 mL, 2 M) and stirred for 5 h. Thereafter, tetraethylorthosilicate (TEOS, 9 g) was added to the homogeneous solution under stirring. The resulting gel was aged at 40 °C for 24 h and finally heated to 100 °C for 24 h. After the synthesis, the obtained solids were calcined under flowing air at 540 °C to decompose the triblock copolymer.

Mesoporous carbon nitride materials were prepared using the mesoporous silica template. In a typical synthesis, 0.5 g of calcined SBA-15 was added to a mixture of ethylenediamine (2.2 g) and carbon tetrachloride (5.4 g). The resultant mixture was refluxed and stirred at 90 °C for 6 h. Then, the dark-brown solid mixture obtained was placed in a drying oven for 12 h and then ground into a fine powder. The template carbon nitride polymer composites were then heat-treated in a nitrogen flow of 50 mL min⁻¹ at 600 °C with a heating rate of 3.0 °C min⁻¹ and kept under these conditions for 5 h to carbonize the polymer. The mesoporous carbon nitride was recovered after dissolution of the silica framework in 5 wt.% hydrofluoric acid, followed by filtration, washing several times with ethanol and drying at 100 °C.

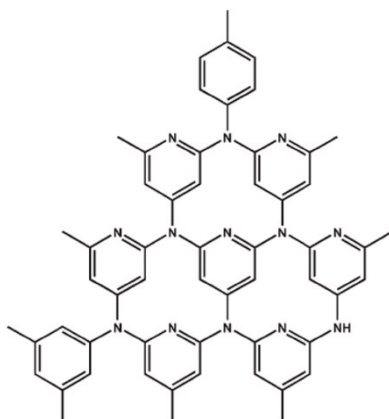
Fabrication of SPME fibers

A MCN suspension was prepared by sonication of 10 mg of MCN powder in 10 mL of water for 30 min, followed by centrifugation at 1000 rpm for 10 min to remove the residual big particles.

The MCN layer was deposited onto stainless steel electrodes by EPD. A 20 V DC was used to drive the particles towards the stainless steel substrate. The distance between two electrodes was 1 cm. The duration of the deposition was 1 h. The same procedure was applied for g-CN coating.

HS-SPME Procedures

The obtained fiber coated with g-CN or MCN was mounted into a homemade SPME device and then was conditioned in the GC injector under helium at 300 °C with gradual rising temperature and held at 300 °C for 2 h. For analysis, all extraction experiments were carried out in a 10 mL working solution, which was introduced to a 20 mL amber vial capped with PTFE-coated septa. Magnetic stirring with a Teflon-coated stir bar was used to agitate the solution at 1000 rpm. A thermostatic water bath was used to control the extraction temperature. To perform the extraction, the g-CN and MCN coated SPME fiber was exposed to the headspace above the water for a certain time. After extraction, the fiber was removed from the vial and immediately inserted into GC inlet for thermal desorption. Before each use, the fiber was conditioned at 300 °C for 10 min.



Scheme S1: Structure of mesoporous carbon nitride.

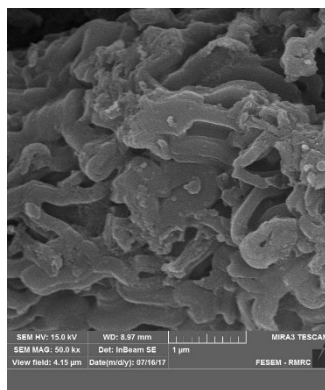


Figure S1: FESEM images of mesoporous carbon nitride coated fiber.

Optimizations of SPME parameters

In order to obtain the best extraction performance, SPME parameters, including extraction temperature, extraction time, salt concentration, desorption time and desorption temperature, were optimized. Prior to optimization, 1000 rpm was fixed as the stirring rate during extraction.

Extraction temperature

Increasing the extraction temperature can accelerate the mass transfer of analytes from aqueous phase to headspace, give a higher concentration of analytes in the headspace and improve adsorption. On the other hand, high extraction temperature can decrease the partition coefficients and subsequent extraction of analytes from headspace to the coating, because of the exothermic nature of the adsorption. Therefore, there is usually an optimum temperature for headspace sampling. According to the results shown in Fig. S2a, S3a and S4a, 60, 40 and 70 °C were selected as the optimal extraction temperatures for PAHs, alkanes and alcohols, respectively.

Extraction time

SPME is an equilibrium-based technique, and the best extraction time should be the equilibrium time. The effect of extraction time on extraction efficiency of PAHs was investigated in a range between 20 and 70 min. The peak area to time profiles for fragrances extracted by the MCN coated SPME fiber is shown in Fig. S2b. Extraction equilibrium for all the analytes was obtained at about 40 min. considering most of the analytes and the total operation time, the extraction time of 40 min was chosen as the optimized extraction time. The influence of extraction time for two alcohols varied between 10 and 60 min and the plots of peak area versus time are shown in Fig. S3b. An extraction time of 40 min was chosen as the optimum value for the following experiments. The influence of extraction time for alkanes was determined from 10 to 50 min and the equilibrium time of 30 min is shown in Fig. S4b.

Salt concentration

The ionic strength of the working solution was adjusted by adding NaCl. Usually, the presence of salt in aqueous solutions increases the ionic strength and decreases the solubility of the analytes in the solution. Thus, the partition coefficients of the analytes between the aqueous solution and headspace are improved. To examine the influence of this parameter on the extraction efficiency, different amounts of sodium chloride, ranging from 0 to 30% (w/v), were added. From the results shown in Fig. S2c, S3c and S4c, 20%, 30% and 20% (w/v) were used as the best amounts of the salt for extractions of PAHs, alcohols and alkanes, respectively.

Desorption temperature and desorption time

The adsorbed analytes should be fully released from the coating fiber to avoid the carryover in subsequent experiments. However, the fiber life-span may be considered. Therefore, both

desorption temperature and time have important effects on extraction recovery and these need to be investigated and optimized. According to the optimization results of PAHs (Figs. S2d and S2e), the desorption temperature of 300 °C and desorption time of 8 min were chosen. For alcohols (Figs. S3d and S3e), the desorption temperature of 300 °C and desorption time of 8 min were selected. Finally, desorption temperature of 260 °C and desorption time of 4 min were selected for the desorption of alkanes (Figs. S4d and S4e).

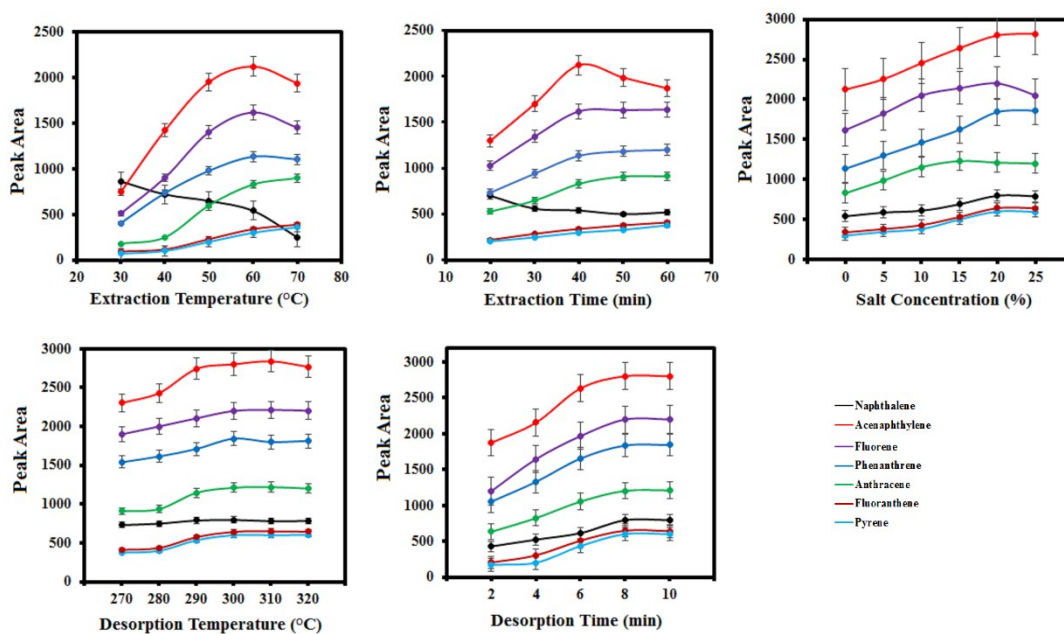


Figure S2: Optimization of SPME parameters for PAHs by employing the MCN coated fiber. (a) Extraction temperature; (b) extraction time; (c) salt concentration; (d) desorption time; (e) desorption temperature.

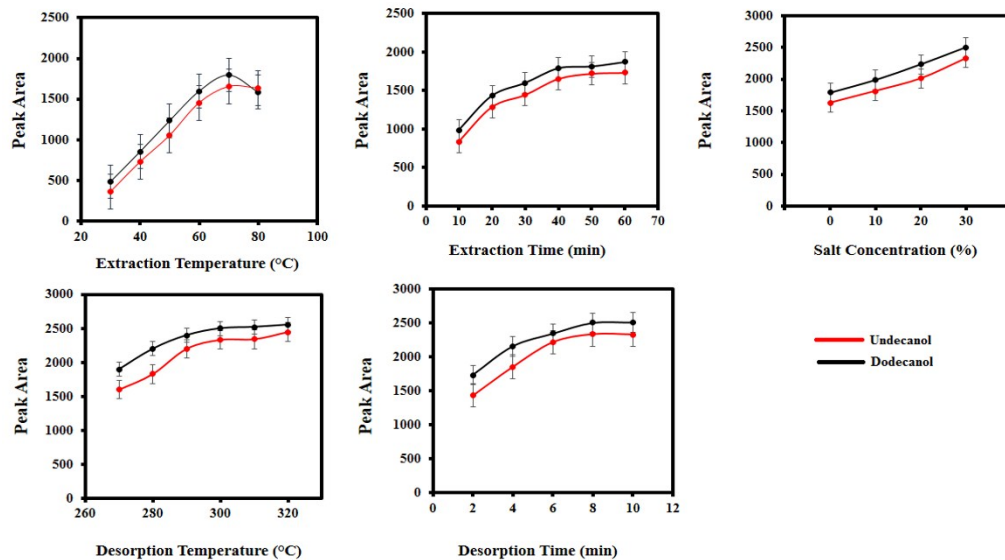


Figure S3: Optimization of SPME parameters for two alcohols by employing the MCN coated fiber. (a) Extraction temperature; (b) extraction time; (c) salt concentration; (d) desorption time; (e) desorption temperature.

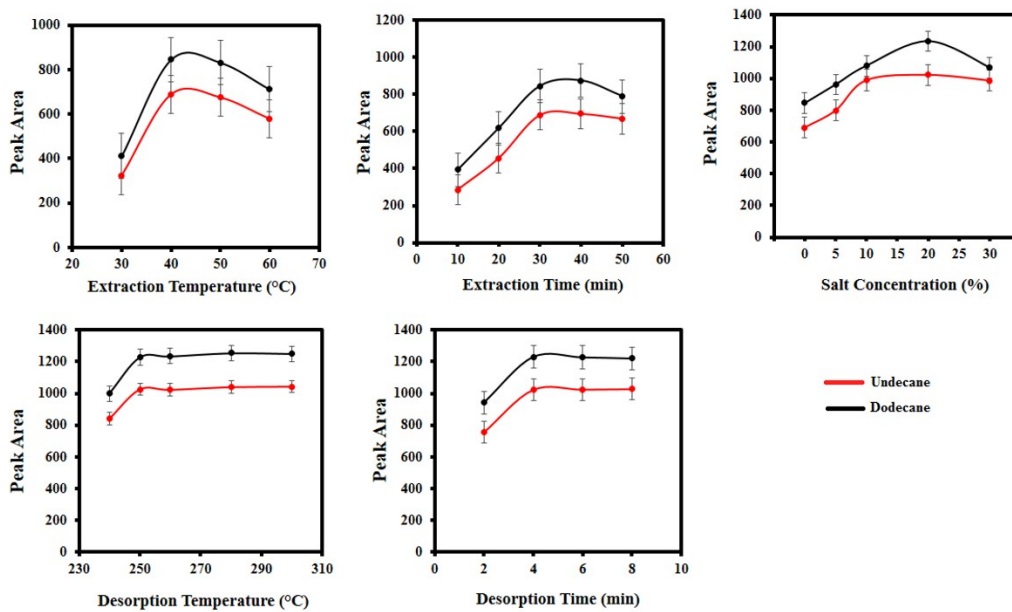


Figure S4: Optimization of SPME parameters for two alkanes by employing the MCN coated fiber. (a) Extraction temperature; (b) extraction time; (c) salt concentration; (d) desorption time; (e) desorption temperature.

Analytical performance of the MCN-coated fiber

Table S1: Analytical parameters of MCN coated fiber for GC-MS determination of PAHs.

Compound	LOD (ng L⁻¹)	LR (ng L⁻¹)	R²	Single fiber (n=6, RSD %)	Fiber-to-fiber (n=3, RSD %)
Naphthalene	1.5	5-2000	0.9992	6.5	8.6
Acenaphthylene	0.2	2-2000	0.9997	3.2	5.4
Fluorene	0.5	2-2000	0.9996	4.3	5.8
Phenanthrene	0.8	2-2000	0.9993	5.1	7.7
Anthracene	1	2-2000	0.9998	4.8	6.8
Fluoranthene	2	30-2500	0.9992	7.1	9.7
Pyrene	2	30-2500	0.9991	6.8	8.4

Table S2: Comparison of different coatings for the SPME of PAHs extraction. (The unit of LODs and LR in some Refs converted to ng L⁻¹)

Coating	Coating method	LOD (ng L ⁻¹)	LR (ng L ⁻¹)	Extraction time (min)	Method	Ref
Graphene	chemical binding to fused-silica substrate	1.52-2.72	5-500	40	HS-SPME-GC/MS	4
polymeric composite incorporating metal organic framework(MOF)		0.11-2.1	20-5000	70	DI-SPME-GC/MS	5
MOF-177	Gluing method	1.2-3.6	2-50	50	HS-SPME-GC/MS	6
Etched Stainless Steel	Etching in Hydrofluoric Acid	240-630	2500-50000	30	DI-SPME-GC/FID	7
g-CN@Graphene	Sol-gel	1-2	10-10000	35	DI-SPME-GC/MS	8
PEDOT@AuNPs ^a	Electrodeposition	2.5-25	100-2500	40	HS-SPME-GC/MS	9
Porous carbon derived from aluminum-based MOF	Sol-gel	5-20	100-12000	20	HS-SPME-GC/MS	10
polymeric ionic liquid	chemical binding	50-250	500-20000	50	DI-SPME-GC/MS	11
Ionic liquid-derived nano-fibrillated mesoporous carbon	Gluing method	0.6-20	10-100000	40	HS-SPME-GC/MS	12
Perhydroxy cucurbit[6]uril	Sol-gel	50-150	100-1000	40	HS-SPME-GC/MS	13
ethoxylated nonylphenol	Sol-gel	50-500	150-200000	25	HS-SPME-GC/MS	14
Ordered mesoporous carbon	Sol-gel	500-1600	1700-100000	50	HS-SPME-GC/FID	15
magnetic carbon nitride nanosheets	-	100-300	500-100000	1	MSPE ^b -GC/MS	16
Mesoporous carbon nitride	EPD	0.2-2	2-2000	40	HS-SPME-GC/MS	This work

^a Poly(3,4-ethylenedioxythiophene) @gold nanoparticles.

^b Magnetic solid-phase extraction

Table S3: Analytical results for determination of PAHs in water samples.

Compound	Sea water			Tap water		
	Origin Concentrations (ng L ⁻¹)	Spiked Concentrations (ng L ⁻¹)	Relative Recoveries %	Origin Concentrations (ng L ⁻¹)	Spiked Concentrations (ng L ⁻¹)	Relative Recoveries%
Naphthalene	8.6	10	90.4	Nd	10	102
Acenaphthylene	Nd	5	106.0	Nd	5	111
Fluorene	17.3	10	98.5	Nd	5	103
Phenanthrene	Nd	5	95.3	Nd	5	96.8
Anthracene	Nd	5	104	Nd	5	92.1
Fluoranthene	103	100	92.8	Nd	50	94.3
Pyrene	148	100	95.6	Nd	50	93.2

Note: Nd stands for not detected.

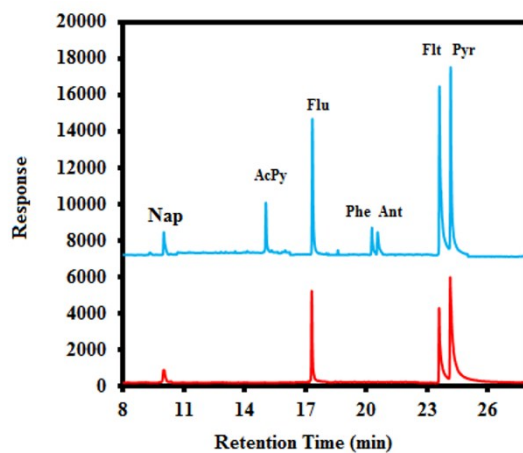


Figure S3: Chromatograms of PAHs from sea water.

Recovery calculation

The %relative recovery (%RR) was calculated by the following equation:

$$\%RR = \frac{C_{found} - C_{real}}{C_{added}} * 100$$

where C_{found} , C_{real} and C_{added} denote the determined concentration of the analytes after spiking of the known amount of the standard into the real sample, the real concentrations of the analytes in the sample, and the spiked concentration into the real sample, respectively. Each treatment was accomplished in triplicates.

Thermal stability of the MCN-coated fiber

The thermal resistance of the fiber coating is a very important parameter for SPME-GC applications. The thermal stability of the MCN coated fiber was investigated by conditioning the fiber at high temperatures of 300, 320 and 350 °C for 1h before extraction. The extraction curves shown in Fig. S6 are stable, which indicates that the MCN is a heat resistant material.

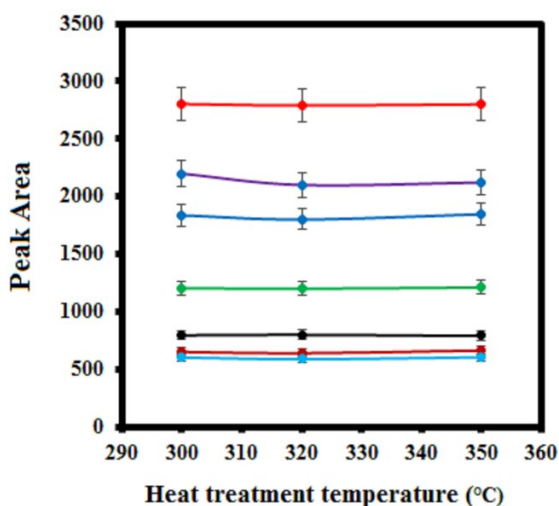


Figure S6: Extraction efficiencies for PAHs after the MCN-coated fiber was treated under different temperatures.

Features and range of application

The sorption performance and mechanism can be evaluated by the in-built N-rich functional groups and electronic delocalization properties endow the CNs with complex sorption mechanism, involving complexation, π - π conjugation, hydrogen bond interaction, electrostatic interaction and hydrophobic effect¹⁷. The sorption mechanism of the sorbent is depended on its structure and surface physicochemical properties, containing specific structure defects, surface functionalities, S_{BET} and isoelectric point (IEP)¹⁷. For example, the surface functionalities ($-\text{NH}_2/-\text{NH}-/= \text{N}-$), favors to adsorb metal ions through complexation or redox reaction¹⁸. In addition, CN with a large number of N atoms in the networks can stabilize metal particles by tight coordination. The aromatic ring would tend to form a delocalized conjugated π structure like that of graphene, which can interact with various metals, double- and triple-bond adsorbates via π - π conjugation, hydrophobic effect and electrostatic interaction¹⁹. Considering the IEP of CN, ionic compounds also can be adsorbed on the sorbent by electrostatic interaction (electrostatic interaction could be favor for direct and in-tube SPME). For example, pure g-CN is negatively charged in neutral solvent and shows better adsorbability for cationic analytes²⁰. Regarding to these features CNs may be useable for direct and in-tube SPME. Moreover, benefiting from the reason of good biocompatibility^{21, 22}, CNs can be used for in-vivo SPME analysis.

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