Monodisperse microporous carbon nanospheres: An efficient and stable solid phase microextraction coating material

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HIGHLIGHTS

- Sol–gel-MMCNSs SPME fiber was prepared and characterized.
- The fiber exhibited superior extraction ability for PAHs and OCPs.
- The fiber was successfully used for the analysis of PAHs and OCPs in real water samples.

GRAPHICAL ABSTRACT
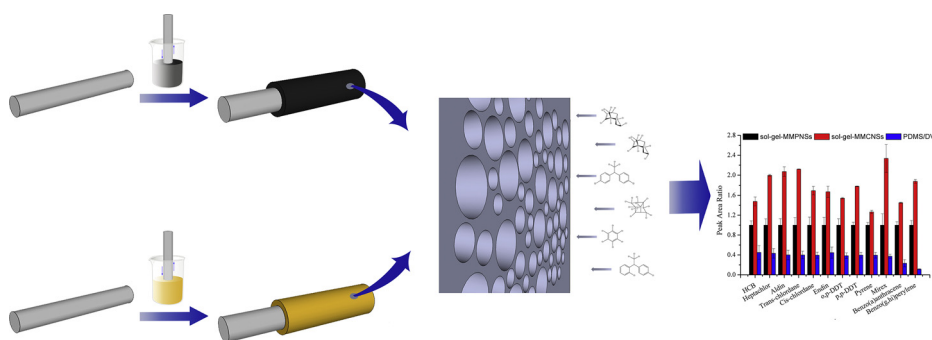
ABSTRACT

The monodisperse microporous carbon nanospheres (MMCNSs) were applied in solid phase microextraction for the first time. The MMCNSs-fiber was prepared by sol–gel technique and good repeatability and reproducibility were obtained, due to the excellent monodispersity of the MMCNSs. The sol–gel-MMCNSs fiber exhibited superior extraction ability for polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs), compared with the commercial polydimethylsiloxane/divinyl-benzene (PDMS/DVB) fiber and the fiber prepared with its precursor, the monodisperse microporous polystyrene nanospheres (MMPNSs). Moreover, the fiber has good thermostability and strong acid/base durability. The sol–gel-MMCNSs fiber was then employed to detect PAHs and OCPs in aqueous samples by combining with gas chromatography–mass spectrometer (GC–MS). Under the optimized conditions, the detection limits of the proposed method ranged from 0.10 to 5.5 ng L^{-1}. Furthermore, the method was successfully utilized for the analysis of PAHs and OCPs in real samples, with satisfactory recoveries in the range of 81.0–120% for the Pearl River water samples and 72.8–118% for the coking wastewater samples.

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1. Introduction

Carbon-based nanoparticles have attracted increased interests in science and engineering due to their unique physical and chemical properties, high surface area, high extraction capacity, lack of internal diffusion resistance, and high surface binding energy [1–4]. As a new kind of carbon nanoparticle, the

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monodisperse porous nanospheres have fascinated the scientific community because their well-defined porous structure, large surface area and unique nanospherical shape make them quite useful in adsorption, drug delivery, energy storage, and catalysis [5–10].

The monodisperse microporous carbon nanospheres (MMCNSs) are kinds of monodisperse porous nanospheres, which was synthesized by the carbonization of monodisperse microporous polystyrene nanospheres (MMPNSs) at 900 °C. The sphere morphology and mesopores are kept after carbonization. Compared to MMPNSs, the MMCNSs possess larger BET surface area (SBET) and total pore volume (Vt) since the pyrolysis generated numerous new micropores [11,12]. The good monodispersity and small particle size also make the MMCNSs more easily to disperse in organic solvents, compared to other carbon materials [11]. In accordance with the above advantages, the MMCNSs have the potential to be an excellent adsorbent, especially in solid phase microextraction (SPME).

SPME is a solvent-free sample preparation technique that integrates extraction, preconcentration and sample cleanup into one step [13,14]. It was developed in the 1990s by Pawliszyn and implemented in analytical practice by his team [15,16]. The fiber coating is the core of the SPME technology which determines the sensitivity and the selectivity of the analytical methods [17–20]. Although several kinds of commercial fibers have been applied in analyses, the drawbacks of the fibers limited their applications, for example, poor thermostability, low mechanical resistance and high cost. Therefore, preparation of new SPME fiber coating to overcome these drawbacks has obtained wide concern [13].

There are two key factors for the preparation of SPME fiber. One is the coating material. The other is the coating technique. Among the materials used as SPME coating, a lot of carbon-based nanoparticles have been utilized to improve the extraction efficiency of SPME fiber, such as carbon nanotubes (CNTs) [21–23], fullerenes [24], graphene [25–28], carbon nanofibers [29,30], carbon nanocones/disks [31], and their functionalized forms [32]. To obtain robust, controllable thickness, and uniform coating, different techniques have been employed for the preparation of SPME fiber, including sol–gel [33–37], electrochemical methods [38–40], in situ growth [41–43], layer-by-layer [25,44,45], as well as physical coating methods [46,47]. In these reported techniques, the sol–gel technology is more popular since it can provide porous structure, high thermal stability and uniform morphology to the fiber coating. In addition, the technique is a convenient way to obtain inorganic and hybrid organo–inorganic polymers with desired shape. However, the technique requires that the nanoparticles can be homogeneously dispersed in the sol solution, and some pretreatments or modifications will be needed for most of the carbon nanoparticles [19].

Hence, for the first time, the MMCNSs based SPME fiber was prepared by sol–gel technology benefiting from the excellent properties of MMCNSs, such as high surface area, good thermostability, and better dispersity. The extraction efficiency, thermostability and acid/base durability of the sol–gel-MMCNSs fiber were compared with those of MMPNSs based SPME fiber (MMPNSs is the precursor of MMCNSs), as well as commercial polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber.

2. Experimental

2.1. Instruments

The gas chromatograph (GC, 6890) equipped with a mass spectrometer (MS, 5975) from Agilent (Palo Alto, CA, USA) was used. The gas chromatograph was operated in splitless mode and helium (99.999%) was used as the carrier gas at a constant flow rate of 1.2 mL min^{-1}. The GC–MS was equipped with an Agilent HP-5 MS column (30 m × 0.25 mm × 0.25 μm) and the column temperature program was as follows: initial temperature 50 °C (held for 0.5 min) to 150 °C at a rate of 20 °C min^{-1}, and again ramped at 15 °C min^{-1} to 250 °C (held for 6 min), finally increased to 270 °C at 30 °C min^{-1} (held for 8 min). The injector temperature was set at 250 °C.

Part of optimization procedures was conducted on a gas chromatograph (7890) equipped with a flame ionization detector (FID) from Agilent (Palo Alto, CA, USA). The injector and detector temperatures were both set at 250 °C. The high-purity nitrogen (99.99%) was used as the carrier gas at a flow rate of 1.2 mL min^{-1}. Hydrogen and air were maintained at flow rates of 30 and 400 mL min^{-1}. The splitless mode was still adapted for gas chromatograph equipped with a HP-5 capillary column (30 m × 0.32 mm i.d. × 0.25 μm film thickness). The GC-FID column temperature program was the same as that of GC–MS.

Both of the instruments (GC–MS and GC-FID) were equipped with the multipurpose samplers (MPS, Gerstel, Germany) for the auto injection.

2.2. Reagents and materials

The styrene (St, 99%), the divinylbenzene (DVB, 80%), and anhydrous aluminum chloride (AlCl$_3$, 99.99%) were purchased from Sigma–Aldrich (Shanghai, China). The sodium dodecyl sulfate (SDS, A.R.) and potassium persulfate (KPS, A.R.) were bought from Tianjin Chemical Reagents Factory (Tianjin, China). The sol–gel reagents were bought from Alfa Aesar (MA, USA), including poly (methylhydrosiloxane) (PMHs, 99%), methyltrimethoxysilane (MTMOS, 97%) and trifluoroacetic (TFA, 99%). Three standard samples of PAHs which contained pyrene, benzo[a]fluoranthene and benzo[ghi]perylene were purchased from Supelco (Bellefonte, PA, USA). Then, 5 mg of pyrene, benzo[a]fluoranthene and benzo [ghi]perylene was added into 10 mL mixture of methanol and methylene chloride (1:1) in turn to get PAHs standard solution (500 mg L^{-1}). Since the extraction efficiencies of commercial PDMS/DVB for heavy PAHs was not satisfactory, it was necessary to investigate the heavy PAHs extraction performance of the prepared fibers. Hexachlorobenzene (HCB, 99.5%), heptachlor (98.5%), aldrin (97.0%), *trans*-chlordance (99.5%), *cis*-chlordance (99.5%), endrin (99.5%), *o,p*-DDT (99.5%), *p,p*-DDT (99.5%) and mirex (99.5%) were purchased from Dr. Ehrenstorfor GmbH (Augsburg, Germany). The organochlorine pesticides (OCPs) standard solution (1000 mg L^{-1}) was prepared by dissolving 10 mg of each OCPs in 10 mL mixed solvent (methanol/methylene chloride, v/v 1:1). The PAHs standard solution and OCPs standard solution were mixed according to the volume ratio of 1:2 to get PAHs and OCPs standard solution. Polycyclic aromatic hydrocarbons (PAHs) which contained naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene and pyrene obtained from Aladdin. The *p*-cresol (99%), 2-nitrophenol (98%), 2,4-dichlorophenol (99%) and 2,4,6-trichlorophenol (99%) was from Alfa Aesar (Beijing, China). Methanol (A.R.), acetone (A.R.), sodium hydroxide (A.R.) and hydrochloric acid (A.R.) were purchased from Guangzhou Chemical Reagent Company (Guangzhou, China). The mixed standard solution of PAHs can be diluted according to the experimental requirements or used directly.

The PDMS/DVB (65 μm) fiber was purchased from Supelco (Bellefonte, PA, USA) and the stainless steel wires were purchased from Component Supply Co. (Fort Meade, MD, USA).

2.3. Preparation of MMPNSs and MMCNSs

MMPNSs and MMCNSs were prepared according to the reported literature [11]. In brief, polystyrene (PS) was synthesized