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In situ solvothermal synthesis of metal–organic framework coated fiber for highly sensitive solid-phase microextraction of polycyclic aromatic hydrocarbons

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ABSTRACT

The present work reported a facile and simple in situ solvothermal growth method for immobilization of metal–organic framework UiO-66 via covalent bonding on amino functional silica fiber for highly sensitive solid-phase microextraction (SPME) of ten polycyclic aromatic hydrocarbons (PAHs) by coupling with gas chromatography–mass spectrometry (GC–MS) analysis. The developed SPME coated fiber has been characterized through SEM, TGA and XRD, confirmed the coating thickness of ~25 μm with high thermal and chemical stability. Under optimized conditions, the obtained method exhibited satisfactory linearity in range of 1.0–5000.0 ng L^{-1} for all the PAHs. The low detection limits were from 0.28 ng L^{-1} to 0.60 ng L^{-1} (S/N = 3). The UiO-66 coated fibers showed good repeatability (RSDs less than 8.2%, $n = 5$) and satisfying reproducibility between fiber to fiber (RSDs less than 8.9%, $n = 5$). This method was successfully used for simultaneous determination of ten PAHs from Minjiang water and soil samples with satisfactory recoveries of 87.0–113.6% and 83.8–116.7%, respectively. Experimental results shows that the chemical bonding approach has dramatically improve the stability and lifetime of pure MOFs coating for SPME in sample pretreatment.

1. Introduction

Solid-phase microextraction (SPME) was first introduced by Arthur and Pawliszyn in 1990, which is an extreme simplicity, sensitivity and solvent-free sampling preparation technique [1]. Nowadays, a number of SPME coatings were commercially available, such as polydimethylsiloxane (PDMS) [2–4], poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) [3,5], polyacrylate (PA) [5], divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) [6,7], and carboxen/polydimethylsiloxane (CAR/PDMS) [8–10], but their performances were not always satisfactoried with some drawbacks such as limited fiber lifetime, poor stability in organic solvents and insufficient selectivity. In order to overcome the above-mentioned problems, much of attempts focused on developing myriad coating materials for SPME.

Nowadays, metal–organic frameworks (MOFs) are an emerging class of crystalline porous hybrid materials consisting of inorganic building blocks and the organic linkers [11]. The unique characteristics of MOFs include good thermal stability and chemical resistance, high specific surface areas, in-pore function, tunable pore size, and out-surface modification [12,13]. Due to these properties, MOFs have been widely applied in gas storage [14], sensing [15], separation [16–18], peptide enrichment and catalysis [19]. Recently, the application of MOFs in SPME has received considerable attention. Up to date, the reported MOFs coating methods for the preparation of SPME coated fibers have mainly involved with physical adhesion, layer-by-layer deposition, in situ hydrothermal growth and covalent bonding approach. For instance, the reported adhesive method for the preparation was to fabricate UiO-66, MOF-177 and MIL-53(M)-coated fiber for the SPME [20–22]. Chang et al. described the preparation of MOFs-coated (MOF-199, ZIF-8 and ZIF-7) SPME fibers by layer-by-layer deposition [23]. And the MOF-199, MIL-88B and MAF-X8 films coating fiber were prepared by in situ hydrothermal growth method [24–26]. Nevertheless, due to lack of stable chemical bonding between the stationary phases and coating fiber surface, the obtained coating fibers by the above

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mentioned methods showed poor stability in organic solvent, the low thermal stability and easy exfoliation from the coatings. So, an effective solution to immobilization of MOFs onto the coating fiber was covalent bonding approach. The main advantage of chemical bonding was it could endow the coatings with enhanced stability and reproducibility. So far, only a few attempts using covalent-bonding fiber for SPME have been reported, such as ZIF-90 [27], hybrid MOF-199/CNTs [28] and MOF-199/graphite oxide hybrid composites coated SPME fibers [29]. However, the reported covalent bonding approaches were still need to put the stainless steel wires or silica-based fibers into mother liquor and react under the harsh or tedious conditions for a long time. Therefore, it is necessary to develop a facile and simple covalent bonding SPME coating preparation method.

In this present work, the UiO-66 SPME coating was fabricated a facile in situ covalent bond method in a serum bottle which only need to react 6 h under the condition of normal pressure and 120 °C oil bath. UiO-66 was built up from zirconium clusters $Zr_6O_4(OH)_4$ and terephthalate ligands [30]. As a cubic rigid 3D porous MOFs, it Possesses large surface area, excellence thermostability and good chemical resistance, being an ideal sorbent for the SPME. Here we reported an easy in situ solvothermal synthesis of robust UiO-66 coating via covalent bonding on amino functional silica fiber for highly sensitive SPME of polycyclic aromatic hydrocarbons (PAHs). PAHs were a group of persistent organic pollutants (POPs) in the environments which have caused worldwide concerns for terrible hazards to public health and environment, because they mainly arise from the incomplete combustion or pyrolysis of organic matter such as oil, coal, petrol, wood, garbage, tobacco, meats or other organic materials [31–33]. As they always existed in trace levels in environmental matrices, it is required and vital to develop efficient preconcentration procedures, high selective, sensitive separation and analysis techniques. The most common analytical methods for PAHs were high performance liquid chromatography (HPLC) and related hyphenated techniques [34,35]; gas chromatography (GC) [36] and gas chromatography–mass spectrometry (GC–MS) [37]. In this work, the UiO-66 SPME coating was coupled with GC–MS to analyze ten PAHs.

During the reaction, the amination silica fiber reacted with the carboxy groups of terephthalic acid via amidation, and the crystal of UiO-66 was fixed on the surface of the silica fiber through the chemical-bonded. Experimental results showed that the chemical bonding approach has dramatically improve the stability and lifetime of pure MOFs coating. Furthermore, owning to the large surface area and unique porous structure of the UiO-66, hydrophobic effect and π–π stacking interaction between the analytes and the framework terephthalic acid molecules, a significant extraction efficiency of the SPME coated fiber for PAHs has been achieved.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used were at least of analytical grade. Zirconium chloride ($ZrCl_4$) and Ten PAHs: fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo (a) anthracene (BaA), chrysene (Chr), benzo(b) fluoranthene (BbF), benzo(k) fluoranthene (BkF), benzo(a) pyrene (BaP) were purchased from J&K Scientific Ltd. (Shanghai, China). Terephthalic acid and 3-aminopropyltriethoxysilane (APTES) (98%) were purchased from Aladdin Reagent Co. (Shanghai, China). Methanol, toluene, ethanol and *N,N′*-dimethylformamide (99%) were purchased from Concord Chemical Research Institute (Tianjin, China). Deionized water (18.2 MΩ cm^{-1}) was prepared with a Milli-Q water purification system (Millipore, USA). Fused-silica fibers (Yongnian Optical Fiber, Handan, China) were used as the substrate to fabricate the UiO-66 bonded fiber for SPME. A 5 μL GC microsyringe (Shanghai Gaoge Industrial and Trade Co. Ltd., Shanghai, China) was used to assemble the SPME device. The stock solution (1000.0 mg L^{-1}) of ten PAHs was prepared by dissolving 25.0 mg of each compound with 25.0 mL of methanol in volumetric flask and stored at 4 °C in darkness. A working standard solution was prepared by stepwise diluting the stock solution with ultrapure water just before use.

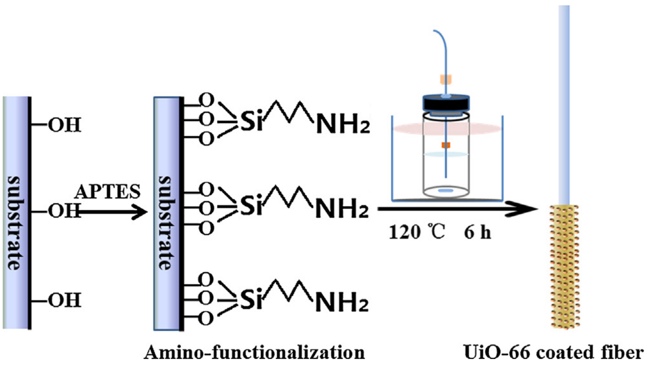

Fig. 1. The schematic fabrication process of UiO-66 coated fiber.

2.2. Instrumentation

Scanning electron microscopy (SEM) images were obtained with a Nova Nano SEM 230 (FEI, USA). Fourier transform infrared (FT-IR) spectra were conducted with a Nicolet 6700 FT-IR spectrophotometer (Nicolet, USA). The surface area and pore diameter were determined with a physisorption analyzer (Micromeritics ASAP 2020 porosimeter, USA) at −196 °C. Before the measurements, samples were degassed in vacuo at 200 °C for at least 480 min. Brunner–Emmet–Teller (BET) method was used to calculate the specic surface areas (SBET) using adsorption data at p/p_0 of 0.05–0.30. The total pore volume (V_t) was estimated from the adsorbed amount at p/p_0 of 0.995. The X-ray powder diffraction (XRD) pattern was determined using a D8 Advance (Bruker, German). The TGA datas of UiO-66 were determined with a DIL402C DTA thermal analysis system (Netzsch, Germany).

2.3. In situ solvothermal growth of bonded fiber

The fused-silica fibers were cut as a length of 20 cm which was used to fabricate the SPME fiber. The schematic fabrication process was shown in Fig. 1.

In detail, firstly, the fused-silica fiber (1.5 cm) was immersed into acetone for 20 min to strip the protective polyimide layer, followed by alkaline treatment using a 1.0 M NaOH solution for 1 h to break the Si—O—Si bonds to form Si—OH groups, washed with deionized water for several times, then dipped the fiber into 0.1 M HCl solution to neutralize the excess NaOH for 0.5 h. The pretreated fused-silica fiber was subsequently rinsed with ultrapure water, and dried at room temperature.

Secondly, the hydroxylated fiber was dipped into an APTES solution for 24 h to react with APTES thoroughly at room temperature. Then the fiber coated with white silanizated APTES layer was washed with toluene and ethanol several times, respectively, and dried at room temperature.

Thirdly, APTES functionalized fiber was vertically immersed into a serum bottle, which was filled with a mixture of $ZrCl_4$ (0.160 g, 0.686 mmol), terephthalic acid (0.114 g, 0.681 mmol) and 0.6 mL acetic acid in 20 mL DMF [38]. The serum bottle was heated at 120 °C in oil bath for 6 h with moderate stirring. During the reaction, the