



Fabrication of cross-linked hydrazone covalent organic frameworks by click chemistry and application to solid phase microextraction



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ABSTRACT

Covalent organic frameworks (COFs) are an emerging class of porous organic frameworks with diverse promising applications. Herein, we presented the first example of cross-linked hydrazone COFs (cross-linked COFs) coating *via* thiol-ene click chemistry for solid phase microextraction (SPME). Strong covalent bonds and interlayer of the prepared networks ensured the adsorption capacity and durability of the novel SPME fiber. π - π conjugated structure existed because of abundant phenyl rings and $-C=N$ groups in the cross-linked COFs. A series of characterizations indicated that the cross-linked COFs possessed large surface areas, high porosities and stabilities as well as hydrophobicities. The fiber was applied to SPME of pesticide residues coupled with gas chromatography with an electron capture detector (GC-ECD). Under the optimum experimental conditions, enhancement factors in the range of 2190–10,998 were obtained, illustrating that the cross-linked COFs possessed remarkable preconcentration ability. The low detection limits of 0.0003–0.0023 ng kg⁻¹ were achieved with relative standard deviations (RSDs) in the range of 3.4–7.6% (intra-batch) and 5.7–11.6% (inter-batch), respectively. Recovery values in the range of 78.2–107.0% were obtained when the SPME-GC method was applied to the analysis of pesticides in cucumber samples.

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1. Introduction

As a potential sample pretreatment technology, solid phase microextraction (SPME) has attracted much attention because it is sensitive and can integrate sampling, extraction, and sample introduction into a single step [1]. Fiber coating is the most important part of SPME, therefore, it is crucial to prepare high-performance coating materials *via* simple and efficient strategies. Nowadays, the fabrication of novel coatings with properties of being simple, robust, long-life, and selective is of great interest. Various types of coatings have been reported, including chemical-bonded graphene [2], sulfonated graphene/polypyrrole [3], ordered mesoporous polymers [4], and highly crosslinked polymer [5] coated fibers.

Recently, porous organic frameworks (POFs) have been regarded as promising materials due to their outstanding properties of high porosity, large surface area, and high stability [6]. Compared with metal organic frameworks (MOFs, another popular porous material fabricated by coordinate bonds) [7], POFs are composed of light elements and connected by covalent bonds,

resulting in their more significant stability in solvents and moisture. Besides, there are a variety of options for organic building blocks to prepare the desired POFs which makes it possible to control the pattern of functional materials [8]. So far, different types of POFs have been synthesized including crystal covalent organic frameworks (COFs) [9], amorphous hyper-cross linked polymers [10], conjugated microporous polymers [11], polymers of intrinsic microporosity [12], and porous aromatic frameworks [13].

Among the various POFs materials, COFs, constructed from B, N, C, and O and linked by robust covalent bonds, have received wide attention due to their desirable properties such as unique ordered channel structure, inherent porosity, well-defined pore aperture, multi-dimension, large surface area, and high stability [14–21]. Generally speaking, COFs are mainly prepared by the polymerization reaction of Schiff bases and boronic acidic derivatives and have been exploited in various applications, including gas storage and separation [22–24], catalysis [20,25,26], and electronics [27–29].

As can be expected, COFs have great potential for adsorption because they can be tailored by selecting suitable building blocks and reaction strategies [17,24,30–32]. For instance, the synthesis and postsynthetic modification of the stable β -ketoenamine TpBD (NH₂)₂ COF were conducted to study its performance of the liquid-phase adsorption of lactic acid in previous work [30]. A survey of

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literature indicated that the application of COFs in the field of sample pretreatment is still under development because of the hindrance of their growth on the substrate of chemical inertia directly. In our previous work, we prepared a hydrazone COF and developed a polydopamine method to introduce COF on a stainless steel fiber, which is the first attempt that COF is immobilized on the chemically resistant substrate for sample preparation [33].

Herein, we developed a facile strategy for the preparation of cross-linked COFs *via* photo-induced thiol-ene click chemistry. The cross-linked COFs were immobilized on the chemically inert stainless steel fiber (SSF) and the prepared coating materials were used for the microextraction of pesticides, which are a threat to humans due to their potential to bioaccumulate. As far as we known, this was the first example that cross-linked COFs was used for the analysis of pesticides *via* SPME pretreatment technology. We hope that our work could inspire researchers to fabricate more well-designed COFs and facilitate the application of COFs in sample pretreatment.

2. Experimental section

2.1. Reagents and materials

Trimesoyl chloride, anhydrous dioxane, mesitylene, hydrazine hydrate, triethylamine (TEA), anhydrous tetrahydrofuran (THF), dopamine hydrochloride, tris (hydroxymethyl aminomethane) hydrochloride (Tris-HCl), 3-aminopropyltriethoxysilane (APTES), 2,2-dimethoxy-2-phenylacetophenone (DMPA), GC-grade methanol, and the standard compounds including 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (*p,p'*-DDE), 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (*p,p'*-DDD), 2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane (*p,p'*-DDT), and chlorpyrifos were purchased from Aladdin (Shanghai, China). Ethanol and acetic acid were purchased from Beijing Chemical Works (Beijing, China). 4-Hydroxyisophthalaldehyde and pentaerythritol tetra(3-mercaptopropionate) (PTM) were obtained from TCI Company (Shanghai, China). Butadiene monoxide was purchased from Alfa Aesar (Beijing, China). Working solutions were prepared by gradually diluting corresponding stock standard solutions with blank cucumber solutions and stored at 4 °C in dark before used. Cucumber samples were purchased from local supermarkets.

2.2. Apparatus and experimental conditions

Fourier-transform infrared (FT-IR) spectra were carried out on a Thermo Nicolet 670 FT-IR instrument (Thermo Nicolet Corporation, USA). The morphology and structure of the fiber coating were observed by scanning electron microscopy (SEM, JSM-6700F, Japan) and transmission electron microscopy (TEM, JEM-2100F, Japan). Thermal gravimetric analysis-derivative thermogravimetric (TGA-DTG) determinations were performed on an STA 449 C thermal gravimetric analyzer (Netzsch, USA). An X-ray photoelectron spectrometer (XPS, Thermo Electron, USA) was used to obtain XPS data. An ASAP 2420 gas adsorption instrument (Micromeritics, Atlanta, USA) was used to record surface area of the fiber coating. Water contact angles were measured with an OCA20 machine (Data Physics, Germany) at saturated humidity with the temperature controlled by a superthermostat (Julabo F25, Germany). All chromatographic measurements were carried out on an Agilent 6890 gas chromatograph (Agilent, Palo Alto, USA) equipped with an electron capture detector (ECD).

2.3. Synthesis of the cross-linked COFs coating

Firstly, the raw material of 1,3,5-benzenetricarbohydrazide was

synthesized according to a previous report with some modifications [34]. The fabrication of 1,3,5-benzenetricarbohydrazide involved the following processes: (a) Synthesis of 1,3,5-benzenetricarboxylic acid triethylester. At first, trimesoyl chloride (0.034 mol) was dissolved in excess ethanol with mechanical agitation followed by the addition of a few drops of trimethylamine. Then the mixture was stirred for 8 h at room temperature and white solid precipitate was obtained. After filtration, the resulting powder was rinsed with water and dried at room temperature. Finally, the crude product was recrystallized from 100 mL of ethanol to yield the target compound. (b) Preparation of 1,3,5-benzenetricarbohydrazide. The obtained 1,3,5-benzenetricarboxylic acid triethylester (0.01 mol) was added into a 1000 mL round-bottom flask containing a solution of 60 mL of ethanol, 60 mL of THF, and 40 mL of $N_2H_4 \cdot H_2O$. The mixture was refluxed at 70 °C for 6 h and then the precipitate was filtered and washed with plenty of water to eliminate the unreacted hydrazine hydrate. The resulting white powder was recrystallized in 80 mL of ethanol to obtain the desired 1,3,5-benzenetricarbohydrazide.

Then, 1,3,5-benzenetricarbohydrazide (0.2 mmol) and 4-hydroxyisophthalaldehyde (0.3 mmol) were added into a three necked round bottomed flask containing a mixture of 5.0 mL of mesitylene, 15.0 mL of anhydrous dioxane, and 0.4 mL of 6.0 mol L^{-1} aqueous acetic acid and the mixture was ultrasonicated for 10 min. Then the solution was dispersed by vigorous agitation with a magnetic stir bar throughout the whole reaction under reflux at 120 °C for 3 days and the whole reaction was kept under the protection of nitrogen. The resulting yellow suspension was filtered and the product was washed extensively with anhydrous dioxane, THF, and acetone in sequence and then dried at 80 °C under vacuum to obtain the hydrazone COFs.

Secondly, butadiene monoxide was used to functionalize the product obtained above through the hydroxyl group of the COFs *via* post-modification. The prepared hydrazone COFs were added into 20 mL of THF followed by the addition of excess butadiene monoxide, after which the mixture was stirred at 80 °C for 6 h to obtain a yellow suspension. After filtration, the solid was washed with THF, acetone, and methanol successively and then the resulting powder was immersed in methanol for 24 h and dried at room temperature followed by drying under vacuum at 80 °C to obtain the yellow powder.

Finally, the cross-linked COFs were prepared by a photo-induced thiol-ene click chemistry synthesis method modified from a previous study [35]. The obtained ethylene functionalized COFs and a certain amount of PTM was dispersed in 10 mL of THF after which DMPA (0.2 wt%) was added into the mixture as the photo-initiator. Then, the reaction system was triggered by UV light ($\lambda = 365 \text{ nm}$) for 5 min and the yielded yellow solid was isolated by centrifugation and rinsed by THF and methanol respectively for several times. The resulting product was dried under vacuum at 80 °C overnight for further experiments.

2.4. Preparation of the cross-linked COFs SPME fiber

Considering that it is difficult to immobilize COFs on the surface of chemical resistant SSF, chemically active polydopamine, a versatile surface modification protocol, was prepared to chemically modify SSF in the following experiments [36]. The detailed preparation process of the cross-linked COFs coated SSF presented herein was illustrated in Fig. 1. Firstly, SSF was etched by aqua regia for 30 min to generate a rough surface with a diameter of 0.2 mm, washed with methanol, and dried in air. By immersing the prepared SSF into a dopamine solution (pH=8.5) at room temperature for 24 h at darkness, thin and surface-adherent polydopamine film was formed on the surface of SSF according to the self-polymerization of dopamine. Then, the obtained fiber was

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