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Polydopamine-supported immobilization of covalent-organic framework-5 in capillary as stationary phase for electrochromatographic separation

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ABSTRACT

Covalent-organic frameworks (COFs) are attractive materials for their fascinating properties, such as rigid structures, exceptional thermal stabilities, low densities, and permanent porosity with specific surface areas, which indicate potential for application in chromatography similar to related metal-organic frameworks (MOFs). However, the utilization of COFs in analytical chemistry is far behind as compared to that of the MOFs due to the challenging work of their immobilization. Here, we have successfully demonstrated the growth of the boron COF-5 on the inner wall of the fused silica capillary by a developed polydopamine-supported method. Combined with the layer-by-layer strategy, multilayer COF-5-coated capillary was obtained. The formation of COF-5 on polydopamine-coated substrate has been confirmed by scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction. A novel stationary phase of COF-5 was developed on the basis of successful growth of COF-5 on polydopamine for open-tubular capillary electrochromatography (OT-CEC). Baseline separation of neutral, acidic and basic analytes was achieved on multilayer COF-5-coated capillary column. The fabricated capillary columns showed high column efficiency (154,060 plates/m for methylbenzene), excellent stability and repeatability. The precision (relative standard deviation (RSD), n = 3) of retention time, peak height, and peak area for tested neutral compounds were in the range of 1.2–1.3%, 1.8–4.2%, and 0.9–2.4%, respectively. To the best of our knowledge, it was the first demonstration that COF-5 was developed as a novel stationary phase.

1. Introduction

Covalent-organic frameworks (COFs), an exciting new type of porous organic materials in which molecular building units are connected through covalent bonds [1–4], has attracted considerable attentions after designed and synthesized [5]. The crystalline nature, high surface areas, permanent porosity together with tailored functionalities and extremely low density offer the COF materials superior potential in diverse applications [6], such as hydrogen storage [7–10], adsorption [11,12], gas separation [13,14], and catalysis [15–17]. It is an interesting work that exploring performances of COFs in the fields of analytical chemistry such as chromatographic separation and extraction like MOFs. However, the utilization of COFs is far behind as compared to that of the related MOFs due to lack of suitable method for immobilization. Very recently, Yang et al. developed facile synthesis of a spherical covalent organic framework, which had been applied to gas chromatography *via* a dynamic coating method [18]. Their pioneering work of the application of COF as stationary phases shows the great potential of COFs for chromatographic separation. Unfortunately, the dynamic coating method for the immobilization of the porous materials mainly relies on physical absorption [19,20], which is unstable for using as stationary phase and adsorbent in the liquid analytical techniques, such as liquid chromatography and capillary electrochromatography (CEC).

Open-tubular capillary electrochromatography (OT-CEC) has attracted great attention because of its advantages such as easy fabrication, good permeability and simple surface modification, especially accessible to employ novel materials as stationary phase, compared with monolithic and packed capillary electrochromatography [21,22]. However, OT-CEC has problems of low sample

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capacity and phase ratio. Several strategies have been reported to address this issue, such as etching the capillary, coating capillary with porous layers and depositing nanoparticle nanoparticles with large surface area as stationary phases [24]. The pioneer works for the application of MOFs in OT-CEC demonstrated the promoting of capillary column technology and the exploring of practical applications about novel porous materials [25,26]. It is possible to broaden applications of COFs since the great potential of COFs for chromatographic separation has been highlighted [18]. We attempt to immobilization of COFs with high surface areas and permanent porosity to overcome the above problems in OT-CEC. However, the stable immobilization of COFs on the inner wall of the capillary is a challenge work because lacking of proper reaction sites in the classical COFs. Recently, COF-5 membrane was grown on the α-Al_2O_3 support by using 3-aminopropytriethoxysilane and 4-formylphenylboronic acid as covalent linkers [27]. However, two steps reaction were required in the prior modification. Besides, the approach was developed to grow COF-5 on commonly used porous α-Al_2O_3 support. Simple and broadly applicable strategy is needed for immobilization of COFs. Our group has much experience in development of immobilizing functional materials for chromatographic separation and selective extraction. We have successfully grown MOF-199 onto the COOH-terminated capillary for electrochromatographic separation by a liquid-phase epitaxy process [28]. We also have carried out the immobilization of monolithic sorbents [29], graphene [30], hydroxyapatite [31], and ZIF-8 [32], by a polydopamine-based surface modification method. These experiences in our previous work for surface modifications encourage us to explore the novel strategy to anchor COFs for new applications especially in capillary electrochromatography.

Bio-inspired polydopamine (PDA) modification method, which played as more and more of seeds coating for chemical functionalization, was firstly developed by Lee et al. [33]. The adhesion of PDA on substrate was resulted by polymerization of dopamine leaving catechol groups and amino groups [33–35]. Recently, PDA has been applied to cells adhesion, proteins immobilization, biominerals formation, and nanoparticles stabilization as a versatile platform for reactions [36–39]. In 2013, Huang et al. successfully attached ZIF-8 membrane layer onto supports by using PDA as a molecular linker to promote the nucleation and crystal growth of the ZIF-8 membrane layer [40]. Our group has developed bio-inspired polydopamine strategy to immobilize graphene, hydroxyapatite and ZIF-8 inside the chemical resistance tube for microextraction and separation [30–32]. Unlike the ZIF frameworks held together by metal-ligand dative bonds, boron COFs are assembled through covalent bonds formed by co-condensation reaction of diboronic acid [1,23,27]. COF-5 is one of the first two boron COFs designed and synthesized by Cote et al. [1]. The condensation reactions of 1,4-diboronic acid (BDBA) and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) containing three catechol groups in each molecule formed the framework of COF-5 [1,23,27]. Its crystal structures are entirely held by covalent bonds between B, C, and O atoms to form rigid porous structures with pore sizes of 27 Å [1]. The dehydration reaction between boric acids groups and catechol groups generates a five-membered BO_2C_2 ring. COF-5 exhibits high thermal stability, permanent porosity, and high surface areas [1], which reminds COF-5 a potential material for utilization as stationary phase like MOFs. With the knowledge of the attendance of catechol groups in both PDA and HHTP, we extended the condensation reaction to BDBA and PDA, which can play as a molecular linker to anchor COFs on the PDA coated substrate.

Herein, we demonstrate the fabrication of the boron COFs coated capillary column for OT-CEC separation by the PDA-supported method. For a proof-of-concept demonstration, we choose the well-known COF-5 as stationary phase. Multilayer COF-5 can be obtained by combining PDA-supported method with the layer-by-layer (LBL) strategy. The fabricated capillary columns are tested by separation of neutral, acidic and basic analytes, and baseline separations are archived. Fused-silica capillaries coated with multilayer COF-5 possess exceptional separation efficiency with high efficiency and excellent stability. The formation of multilayer COF-5 anchored on PDA layer is characterized by scanning electron microscopy (SEM), Fourier transforms infrared spectroscopy (FT-IR), and X-ray diffraction (XRD). To the best of our knowledge, there is no report on the immobilization of boron COFs by using PDA as a molecular linker as novel stationary phases. Growth of COF-5 on PDA layer, which paves the way for immobilization of boron COFs on versatile substrates, will extend the application of COFs to more analytical fields for the application of COFs.

2. Experimental

2.1. Chemicals and materials

The reagents used in the experiments were of analytical or chromatographic grade. Dopamine was purchased from Sigma-Aldrich (MO, U.S.A.). Methylbenzene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene, 4-methylbiphenyl, 1,3,5-trimethylbenzene and 1,4-dioxane were obtained from Aladdin (Shanghai, China). 1,4-Diboronic acid (BDBA) and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) were bought from TCI (Shanghai, China). 4-Aminobenzoic acid, benzoic acid, 3,5-dimethylbenzoic acid, *N,N*-dimethylbenzenamine, phenylamine, 2-phenylethylamine, naphthalene and sodium phosphate dibasic dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$) were commercially available from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Bare fused-silica capillaries with a dimension of 50 μm i.d. × 360 μm o.d. were obtained from Polymicro Technologies (Phoenix, AZ, USA).

2.2. Instrumentation

The morphology observation of prepared capillary column was performed on a Carl Zeiss Ultra Plus Field Emission scanning electron microscope (FESEM, Carl Zeiss, Germany) at an accelerating voltage of 20 kV. Fourier translation infrared spectra (FT-IR) were collected from a Thermo Nexus 470 FT-IR system (MA, UAS). X-ray diffraction patterns were determined on a X-ray diffractometer (X'Pert PRO, PANalytical B.V., the Netherlands) with radiation of a Cu target (Kα, λ = 0.15406 nm). Deionized water used was purified with a Milli-Q system (MA, USA). All CEC separations were performed on an Agilent 7100CE system (Waldbronn, Germany) equipped with an auto-sampler, a diode array detector, a temperature controlled column compartment and a chromatographic workstation (Chemistry Station, USA) for data acquisition and treatment. Prior to the first use, the coated capillary column was rinsed by buffer solution (5 min).

2.3. Standard solutions and buffer solutions preparation

Standard solutions of 3 mg/mL of the analytes were prepared by dissolving in methanol and were refrigerated at 4 °C. The running buffer was prepared by mixing 10 mM Na_2HPO_4 at different pH values with an appropriate amount of methanol. The pH value of the phosphate solution was adjusted to 6.0–9.0 using phosphoric acid solutions. Prior to CEC analysis, the solutions were diluted to the appropriate concentration to form the working sample solution, which was degassed under ultrasonication before injection. All these solutions were filtered by syringe-driven filter before use.