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Metal-organic framework polymethyl methacrylate composites for open-tubular capillary electrochromatography

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ABSTRACT

Metal-organic frameworks (MOFs) are attractive as novel separation medium due to their distinguished properties including large surface area, accessible tunnels and diverse structures. Here, we report the incorporation of MOF CAU-1 (CAU = Christian-Albrechts-University) into polymethyl methacrylate (PMMA) to produce a new composite (CAU-1@PMMA), and the fabrication of CAU-1@PMMA coated capillary for open tubular capillary electrochromatography (CEC). CAU-1 contains unprecedented $[Al_8(OH)_4(OCH_3)_8]^{12+}$ clusters connected by twelve aminoterephthalic acid linkers, and is highly porous and stable in a variety of buffer solutions. The incorporation of CAU-1 into PMMA not only increases surface area, but also electroosmotic flow (EOF). As a result, the CAU-1@PMMA coated capillary column gives higher column efficiency, larger column capacity, and shorter separation time for baseline separation of two groups of aromatic carboxylic acids than the PMMA coated capillary column. Besides, the incorporation of CAU-1 also improves the resolution for the CEC separation of basic sulfa drugs and structurally related peptides. The run-to-run, day-to-day and column-to-column precision for the EOF of CAU-1@PMMA coated capillary column is 0.3%, 0.4%, and 2.2% (relative standard deviation), respectively. The results show that MOFs composites are promising stationary phases for CEC applications.

1. Introduction

Open tubular capillary electrochromatography (OT-CEC) has received great attention due to its advantages of ease of column preparation, no requirements of end frits and particles packing, variety and availability of surface modification and less bubble formation than packed capillary electrochromatography [1]. Nevertheless, it suffers from relatively low column capacity and phase ratio due to the typical small surface area of the coating [2]. To date, several methods have been reported to address this issue, such as porous layers [3,4], sol–gel techniques [5,6] and etching [7,8]. Besides, application of nanoparticles with large surface area as stationary phases, such as lipoprotein particles [9–11], silica particles [12,13], multi-walled carbon nanotubes [14,15], graphene and graphene oxide [16], is an effective way to increase the phase ratio of OT-CEC column.

Metal-organic frameworks (MOFs) are intriguing microporous crystalline materials consisting of clusters or chains of metal ions connected by organic ligands and offer outstanding properties such as large surface area, diverse structure and accessible tunnels and cages [17–19]. These unique features make MOFs attractive as novel separation media in separation sciences [20–45]. So far, MOFs have been used as sorbents for sampling [20], solid-phase extraction [21–24], micro solid-phase extraction [25] and solid-phase microextraction [26–28], as stationary phases for capillary gas chromatography [29–34] and high-performance liquid chromatography [35–38], and as pseudostationary phase for capillary electrokinetic chromatography [39]. In addition, MOFs composites, which combine the outstanding functionality of MOFs and the original nature of the matrix with additional merit of easy-to-handle have been shown to be promising in separation science [40–44]. However, the utilization of MOFs or their composites in OT-CEC has not been reported up to now.

Herein, we report our primary attempt to incorporate MOF CAU-1 (CAU = Christian-Albrechts-University) into polymethyl methacrylate (PMMA) to fabricate a new composite (CAU-1@PMMA) to improve the column phase ratio for OT-CEC. CAU-1 contains unprecedented $[Al_8(OH)_4(OCH_3)_8]^{12+}$ clusters connected by twelve aminoterephthalic acid linkers, and is highly porous and stable in a variety of buffer solutions. CAU-1 possesses two kinds of cavities with effective diameters of approximately 1.00 and 0.45 nm and has large Langmuir surface area of nearly 1700 $m^2\ g^{-1}$ [46]. Polymethacrylate is often used as the matrix for incorporating nanoparticles to produce various composites for CEC [47,48,49]. In this work, we find that the incorporation of CAU-1 into PMMA increases the column capacity and electroosmotic flow (EOF),

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making the column more suitable for the separation of acidic compounds in CEC. Moreover, the incorporation of CAU-1 into PMMA also improves the separation of basic sulfa drugs and structurally related peptides.

2. Experimental

2.1. Chemicals and reagents

All reagents and chemicals used were at least of analytical grade. Ultrapure water (Wahaha, Hangzhou, China) was used throughout all experiments. Methyl methacrylate (MMA), γ-methacryloxypropyltrimethoxysilane (γ-MAPS), methyleneglycol dimethacrylate (EDMA) and aminoterephthalic acid were purchased from Alfa Aesar (Ward Hill, MA, USA). Azobisisobutyronitrile (AIBN), $Al(NO_3)_3{\cdot}9H_2O$, benzoic acid, aspirin, *m*-phthalic acid, *o*-phthalic acid, sulfamethazine, sulfanilamide, sulfadiazine and sulfamethoxazole were purchased from Aladdin (Shanghai, China). Thiourea, dimethyl sulfoxide (DMSO), sodium dihydrogen phosphate and disodium hydrogen phosphate were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Acetonitrile (ACN) and methanol (MeOH) were from Concord Technology (Tianjin, China). Ibuprofen, naproxen and ketoprofen were from Zhejiang Xianju Pharmaceutical Corporation (Xianju, China). Fused-silica capillaries (375 μm o.d. × 75 μm i.d.) were from Yongnian Optic Fiber Plant (Handan, China).

2.2. Synthesis of CAU-1

CAU-1 was synthesized according to Ahnfeldt et al. [46]. Typically, $Al(NO_3)_3{\cdot}9H_2O$ (1.92 mmol) and aminoterephthalic acid (0.516 mmol) were mixed with MeOH (5.0 mL) in a Teflon-lined bomb. The Teflon-lined bomb was then sealed and heated at 125 °C in the oven for 8 h. The resultant yellow crystal CAU-1 was washed with MeOH and water, and then collected by centrifugation at 10,000 rpm for 5 min. The procedure was repeated three times to remove the excessive aminoterephthalic acid from CAU-1, and then the crystal CAU-1 was dried at 250 °C in vacuum over night. Finally, the yellow solid was characterized by X-ray diffraction (XRD) spectrometry.

2.3. Fabrication of CAU-1 incorporated open-tubular capillary column

Firstly, the fused silica capillary was treated by rinsing with 1.0 M NaOH for 3 h, ultrapure water for 1 h, 0.1 M HCl for 1 h, methanol for 1 h, sequentially, and then dried with a flow of nitrogen. Secondly, the treated capillary was filled with a solution of γ-MAPS in MeOH (1/1, v/v) with both ends sealed, kept at 40 °C for 16 h, then washed with MeOH to remove the residual γ-MAPS and dried with a flow of nitrogen. Thirdly, CAU-1 was suspended in DMSO at a concentration of 5 mg mL^{-1} via ultrasonication for 20 min. MMA (35 μL), EDMA (400 μL) and AIBN (1 mg) were added into the CAU-1 solution (1.2 mL) and sonicated for 5 min. The resultant solution was then filled into the capillary and most of the solution was purged out of capillary by blowing nitrogen at 40 kPa for 30 min, leaving the capillary wall with a thin layer of the solution. Finally, both ends of the capillary were sealed for polymerization at 70 °C for 16 h. The obtained capillary was washed with MeOH to remove the unreacted monomers. The pure PMMA column was synthesized in parallel by adding the same amount of MMA, EDMA and AIBN into DMSO (1.2 mL). The PMMA and CAU-1@PMMA materials were also prepared in 1.5 mL centrifuge tube, washed with MeOH, and dried at 150 °C over night for XRD characterization.

2.4. Characterization

The XRD patterns of the synthesized CAU-1, CAU-1@PMMA and CAU-1 treated in different buffers were recorded with a D/max-2500 diffractometer (Rigaku, Japan) using Cu Kα radiation (λ = 1.5418 Å). Three buffers were involved for the treatment of CAU-1, namely, citrate sodium-citrate acid (0.2 M, pH 3.0), HAc-NaAc (0.2 M, pH 4.3), and phosphate buffer solution (PBS, 0.2 M, pH 3.0 and 9.0). The CAU-1 was dispersed in those buffers (5 g L^{-1}) at room temperature for 24 h, then the suspensions were centrifuged at 10,000 rpm for 10 min, and the solid was collected and washed with ultrapure water for three times and dried at 120 °C over night for XRD measurements.

The high resolution transmission electron microscopy (HRTEM) image of CAU-1 dispersed in the prepolymer was recorded on a JEM-2100F field emission transmission electron microscope (JEOL, Japan) operating at a 200 kV accelerating voltage. Zeta potentials of the CAU-1 (0.4 g L^{-1}) in ultrapure water and PBS with different pH were measured on a Zeta potential analyzer (Brookhaven Instruments Co., Holtsville, NY, USA). Scan electron microscopy (SEM) images of PMMA and CAU-1@PMMA were recorded on a SS-550 scanning electron microscope (Shimadzu, Kyoto, Japan) at 15.0 kV. BET (Brunauer–Emmett–Teller) surface area of the materials were recorded on an adsorption instrument (ASAP 2020/Tristar 3000, Micromeritics, USA).

2.5. OT-CEC and capillary electrophoresis (CE) separation

OT-CEC and CE separations were performed on a P/ACETM MDQ capillary electrophoresis system (Beckman, Fullerton, CA, USA) equipped with a DAD detector. The mobile phase, composed of appropriate amount of buffer solution, water and ACN, was fresh-made and filtered through a 0.45 μm filter before use. The bare capillary column, CAU-1@PMMA and PMMA open-tubular capillary columns were rinsed with MeOH (15 min), ultrapure water (4 min), and mobile phase (2 min) before the first use, and with MeOH (4 min), ultrapure water (2 min) and buffer (2 min) between consecutive runs. The standard solutions were injected hydrodynamically at 0.5 psi for 3 s. The electropherograms of aromatic acids, nonsteroidal anti-inflammatory drugs, sulfa drugs and peptides were monitored at 244 nm, 214 nm, 254 nm and 214 nm, respectively. Thiourea (2 mg L^{-1}) was used as the EOF marker.

3. Results and discussion

3.1. Characterization of CAU-1 and CAU-1@PMMA

The XRD pattern of the synthesized CAU-1 crystals is in good accordance with the simulated data, indicating the successful synthesis of CAU-1 (Fig. 1A). CAU-1 displays good stability in the examined buffers as all the XRD peaks belonging to CAU-1 remain after treatment in different buffers (Fig. 1A). The prepared CAU-1 nanocrystals are cuboid (248 nm × 509 nm) (Fig. 1C). The transparent PMMA prepolymer solution (Fig. 1B-a) became homogeneous and yellow after the addition of CAU-1 under ultrasonication (Fig. 1B-b). The resulting CAU-1@PMMA composite is homogeneous (Fig. 2A-b). The above results show the good dispersibility of the nanosized CAU-1 in DMSO and the mixture of MMA, EDMA and DMSO.

The incorporation of CAU-1 into the CAU-1@PMMA composite was ascertained by the homogeneous yellow color (Fig. 2A-b) compared with the PMMA polymer (Fig. 2A-a), and the appearance of the XRD pattern of CAU-1 in CAU-1@PMMA (Fig. 2B). The TEM image of CAU-1@PMMA also suggests the existence of CAU-1