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In situ rapid preparation of homochiral metal-organic framework coated column for open tubular capillary electrochromatography

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ABSTRACT

Fabricating metal-organic frameworks (MOFs) with the use of nucleating agents in the microenvironment have attracted increasing attention recently. Herein, a simple and rapid synthesis method was developed to in situ fabricate homochiral MOF $[Zn(s\text{-}nip)_2]_n$ in the capillary inner wall by using ZnO nanoparticles as efficient nucleating agents for open tubular capillary electrochromatography (OT-CEC) separation of monoamine neurotransmitters enantiomers of epinephrine, isoprenaline and synephrine, the diastereoisomers of ephedrine and pseudoephedrine, the isomers of nitrophenols and analogues of bisphenols with good resolution. The relative standard deviations (RSDs) for the analytes migration time of intra-day, inter-day and column-to-column were in the range of 0.8–2.1% ($n = 10$), 0.3–3.2% ($n = 3$) and 3.2–9.3% ($n = 3$), respectively. Additionally, the homochiral MOF $[Zn(s\text{-}nip)_2]_n$ coated capillary column could be successively used over 260 runs without observable change in the separation efficiency.

1. Introduction

Metal-organic frameworks (MOFs), a novel class of microporous crystalline materials consisting of metal ions and organic ligands, have attracted increasing attention owing to their specific properties of large specific surface areas, controllable synthesis and flexibility of the pore sizes [1,2]. Owing to their unusual properties, they have been increasingly in demand in application in gas storage [3,4], asymmetric catalysis [5,6], sorption [7] and separation [8–10]. In particular, MOFs as novel stationary phases for chromatography separation have received increasingly attention recently. For example, various MOFs have been explored as stationary phases for high performance liquid chromatography (HPLC) [11–15] and gas chromatography (GC) [16–19]. Besides, MOFs have also been revealed to be promising stationary phase for open tubular capillary electrochromatography (OT-CEC) [20–22]. Currently, most approaches used for fabricating MOF coated capillary columns for OT-CEC were off-line uncontrollable procedures, which usually need an extra-column synthetic procedure. Therefore, in situ fabricating functional MOFs as stationary phase for OT-CEC will be a good choice.

The researchers have been trying to develop simple, gentle and in situ MOF fabrication methods and applied them to prepare MOF coated capillary columns for OT-CEC separation. For example, our group developed an in situ, layer-by-layer self-assembly approach to fabricate MIL-100(Fe) coated capillary columns for OT-CEC separation of some neutral, acidic and basic analytes [20]. And then we further prepared a homochiral MOF AlaZnCl coated capillary column at room temperature by using this in situ, layer-by-layer self-assembly approach and applied it in the enantioseparation of four monoamine neurotransmitters and two amine drugs [23]. Chen et al. also carried out the growth of HKUST-1 on the inner wall of capillary by using liquid-phase epitaxy process at room temperature for the separation of some substituted benzene [24]. The above in situ MOF preparing methods to a certain degree simplified the preparing process compared to the off-line preparing methods. Even so, multiple fabrication steps, complicated column preparation process and relatively long preparation time (more than 26 h) are still needed, which might influence the stability and reproducibility of the fabricated columns. Therefore, more simple fabrication methods should be explored to further simplify the preparation process, which would further facilitate the potential application of MOFs in OT-CEC.

Recently, heterogeneous nucleation to seed crystal growth MOF has attracted much attention [25–27]. Relative to traditional solvothermal methods, the use of nucleating agents in the MOF preparing process could significantly reduce the synthesis time. For

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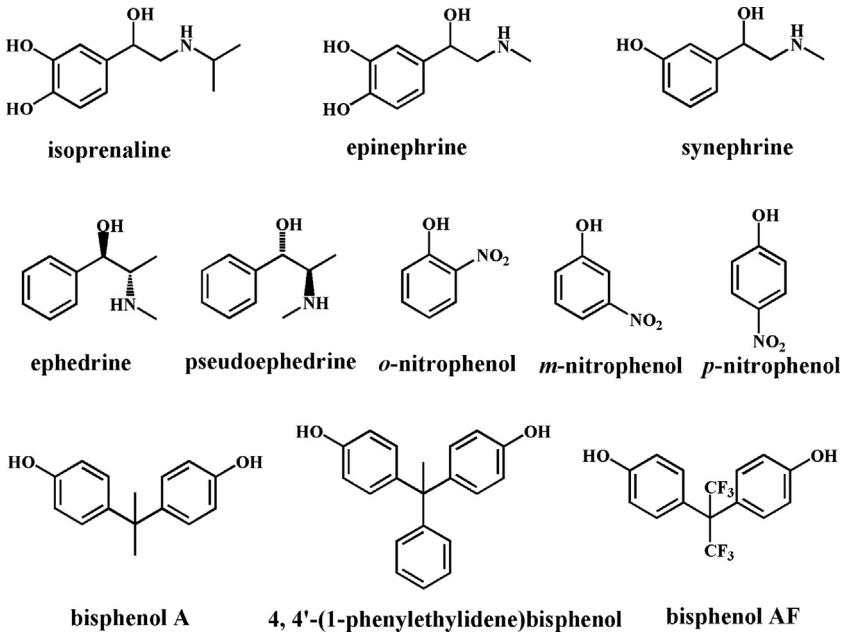

Fig. 1. Chemical structures of tested model analytes.

example, Paolo et al. demonstrated the synthesis of Zn-based MOFs using ZnO nanoparticles as nucleating agents with quite short processing time (MOF crystals in less than 30 min) [28]. Inspired by this work, herein, we firstly reported the use of ZnO nanoparticles as efficient nucleating agents for in situ rapid synthesis of homochiral MOF $[Zn(s\text{-}nip)_2]_n$ in the capillary inner wall for OT-CEC separation. This developed method allows in situ synthesis of homochiral MOF $[Zn(s\text{-}nip)_2]_n$ in the capillary inner surface in 1 h. Moreover, the obtained rapid growth $[Zn(s\text{-}nip)_2]_n$ showed good solvent stability in electrolyte solution and organic solvents and also good thermostability, which offers its potential application in separation science. The obtained homochiral MOF $[Zn(s\text{-}nip)_2]_n$ coated capillary column in this work was applied in the OT-CEC separation of three kinds model analytes including the enantiomers of three monoamine neurotransmitters, the diastereoisomers of ephedrine and pseudoephedrine, the isomers of nitrophenols and analogues of bisphenols.

2. Experimental

2.1. Chemicals and materials

ZnO nanoparticles and 3-glycidoxypropyltrimethoxysilane (GLYMO) were obtained from Sigma–Aldrich (MO, USA). NaOH and HCl were obtained from Chengdu Kelong chemical Co., Ltd. (Chengdu, China). $Zn(NO_3)_2{\cdot}6H_2O$, methanol, ethanol, acetonitrile, formamide, L-Histidine, *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, bisphenol A, bisphenol AF and 4, 4′-(1-phenylethylidene) bisphenol were commercially available from Tianjin Guangfu Co., Ltd. (Tianjin, China). 1, 8-naphthalic anhydride was purchased from 9 Ding Chemistry Co., Ltd. (Shanghai, China). Borate was purchased from Xi'an Chemical Plant (Xi'an, China). Isoprenaline and synephrine were bought from J&K Scientific LTD. (Beijing, China). Ephedrine, pseudoephedrine and epinephrine were purchased from national Institutes for Food and Drug Control (Beijing, China). Chemical structures of the model analytes are shown in Fig. 1. Unless otherwise stated, all chemicals and reagents used were analytical grade and used without further purification. Fused silica capillary (375 μm o.d. × 75 μm i.d.) was purchased from Yongnian Photoconductive Fiber Factory (Hebei, China). Ultrapure water was used throughout the experiment.

2.2. Apparatus and characterization

Scanning electron microscopy (SEM) images were recorded on a JSM-5600LV emission scanning electron microscope (JEOL, Japan). ^{1}H NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometer using DMSO-d_6 as solvent (Chemical shifts (H) are reported in ppm) (Bruker, German). Powder X-ray

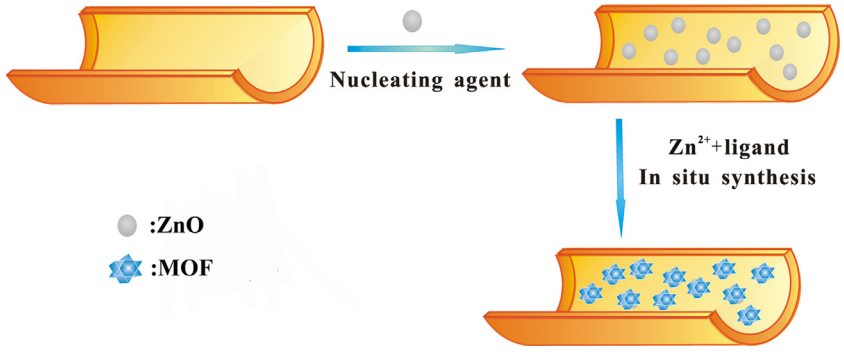

Fig. 2. Schematic diagram for the preparation process of $[Zn(s\text{-}nip)_2]_n$ coated capillary column.