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Thin metal organic frameworks coatings by cathodic electrodeposition for solid-phase microextraction and analysis of trace exogenous estrogens in milk

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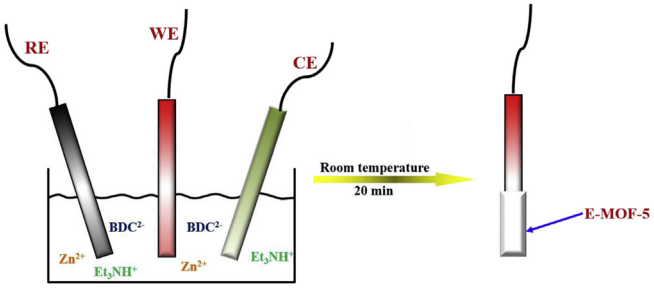
HIGHLIGHTS

- $(Et_3NH)_2$-MOF-5 coated SPME fiber was fabricated *via* a cathodic electrodeposition approach.
- $(Et_3NH)_2$-MOF-5 coated fiber showed good stability and selectivity for SPME of exogenous estrogens.
- One $(Et_3NH)_2$-MOF-5 coated fiber can be prepared in 2.5 min.
- Low detection limits and good repeatability for estrogens was achieved by the fiber.

GRAPHICAL ABSTRACT



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ABSTRACT

Cathodic electrodeposition (CED) has received great attention in metal-organic frameworks (MOFs) synthesis due to its distinguished properties including simplicity, controllability, mild synthesis conditions, and product continuously. Here, we report the fabrication of thin $(Et_3NH)_2Zn_3(BDC)_4$ (E-MOF-5) film coated solid phase microextraction (SPME) fiber by a one-step in situ cathodic electrodeposition strategy. Several etched stainless steel fibers were placed in parallel in order to achieve simultaneously electrochemical polymerization. The influence of different polymerization parameters Et_3NHCl concentration and polymerization time were evaluated. The proposed method requires only 20 min for the preparation of E-MOF-5 coating. The optimum coating showed excellent thermal stability and mechanical durability with a long lifetime of more than 120 repetitions SPME operations, and also exhibited higher extraction selectivity and capacity to four estrogens than commonly-used commercial PDMS coating. The limits of detection for the estrogens were 0.17–0.56 ng mL^{-1}. Fiber-to-fiber reproducibility ($n = 8$) was in the respective ranges of 3.5%–6.1% relative standard deviation (RSD) for four estrogens for triplicate measurements at 200 ng mL^{-1}. Finally, the (E-MOF-5) coated fiber was evaluated for ethinylestradiol (EE2), bisphenol A (BPA), diethylstilbestrol (DES), and hexestrol (HEX) extraction in the spiked milk samples. The extraction performance of this new coating was satisfied enough for repeatable use without obvious decline.

1. Introduction

Solid-phase microextraction (SPME), developed by Pawliszyn and co-workers in 1990s [1], is a simple, powerful, time-saving, and

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solvent-free sample preparation technique due to its integration of sampling, isolation, enrichment, and injection into one step [2–5]. It has been widely applied for the separation and enrichment of various organic/inorganic compounds from food [4], environmental [6], and biological [7] samples at trace level. The fiber coating is acted as the extraction/desorption phase of the target compounds, so the coating material is crucial in SPME development. Only a few types of materials such as polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB), carboxen (CAR), carbowax (CW), and their composites were commercially available for SPME nowadays [8,9]. However, caused by the unsatisfied thermal and/or chemical stability, insufficient selectivity, and limited reuse times of these coating materials, their practical applications were frequently restricted.

Metal organic frameworks (MOFs) are porous and crystalline materials which consisting of chains or clusters of metal ions connected by organic linkers and present outstanding properties such as the flexible pore size and shape, diverse structure, and large surface area [10–14]. These excellent characteristics make MOFs promising for application in SPME. As we known, the applications of MOFs in SPME have been reported with different fabrication strategies such as in situ hydrothermal growth and physical adhesion strategies [2,15–17]. Yan's group reported the fabrication of MOF 199 film coated SPME fiber by in situ hydrothermal growth for gaseous benzene separation and determination [15]. Li's group reported the fabrication of MOF 199/graphite oxide film coated SPME fiber via a physical adhesion strategy for organochlorine pesticides analysis [17]. However, when it comes to the synthesis of MOFs, high temperature, and harsh pH conditions were usually needed. Moreover, MOFs coatings prepared with these methods have met some troubles such as uncontrolled molar mass and composition and time-consuming preparation procedures. Furthermore, high coating thickness would result in the insufficient pore accessibilities for analytes and potential residual of target compounds even after time-after-time desorption procedures. It is expected urgently that MOFs with improved homogeneity, mass transferability, accessibility, and selectivity. In this regards, it is of significance to developing more controllable and simple fabrication method to prepare MOFs coatings at ambient temperature and neutral pH.

Electrochemical polymerization methods have drawn a lot of attention in the last decade. Compared with physical adhesion, sol-gel technology, and layer-by-layer chemical bonding coating preparation methods [2,15–18], electrochemical polymerization has many advantages such as mild preparation conditions, flexible, simple setup, and unbreakable metal support to provide coatings with variable thickness. By this strategy, SPME coating can be directly in situ fabricated on the surface of a metal wire substrate via a one-step electrochemical polymerization strategy. Unbreakable metal fibers substrate showed high thermal stability, long life span, good conductivity, and high stability to the organic solvents. Moreover, electrochemical polymerization conditions such as applied potential and synthesis time can be easily controlled by a three-electrode system to achieve stable and reproducible SPME coatings. Recently, electrochemical polymerization methods have been applied for preparation of metal organic framework-polyaniline nanocomposite, conductive polymers, metal oxides and carbon nanotubes [19–22]. Gascon's group reported the fabrication of MOFs on the Pt mesh by electrodeposition which provided us a useful guidance to use electrochemical polymerization method to prepare novel MOF SPME coating [23].

Estrogens have attracted a great deal of scientific and political attention due to their presence in food and their estrogenic activities [24]. The prominent compounds could enter the human body through a food chain, and interfere with the normal functions of the endocrine systems [25]. These estrogens play an important role in mineral-, fat-, sugar- and protein-metabolization in the human body; even cause tumors such as the breast cancer and prostate cancer [26,27]. Especially, some exogenous estrogens such as ethinyloestradiol (EE2), bisphenol A (BPA), diethylstilbestrol (DES) hexoestrolum (HEX) have a deeper influence on human health [28]. For the purpose of fattening animals, large amounts of estrogens are illegally used, which can then be transported in blood and finally excreted in milk [29]. Thus, milk is an important product being threatened by the use of estrogens. Thus, the development of highly sensitive and selective methodologies for determination of estrogens in milk is of great significance for food safety supervision.

The aim of this work is to fabricate novel $(Et_3NH)_2Zn_3(BDC)_4$ (E-MOF-5) layer on an etched stainless steel fiber for the SPME of the four exogenous estrogens from milk samples with good lifetime and efficiency. E-MOF-5 ($(Et_3NH)_2Zn_3(BDC)_4$, BDC = 1,4-benzenedicarboxylate) was built up from zinc-centered trimers and terephthalate organic linkers. The large surface area (919 $m^2\ g^{-1}$) [23], good thermal, and solvent stability makes E-MOF-5 a potential novel sorbent for the SPME of estrogens. Here, we first report in situ cathodic electrodeposition of E-MOF-5 films on firm stainless steel fibers for the SPME of estrogens from milk samples. Parameters such as extraction temperature, extraction time, and desorption time were optimized. Moreover, the E-MOF-5 coated fibers were applied for the SPME of estrogens in milk samples.

2. Experimental

2.1. Chemical reagents and materials

Ethinyloestradiol (EE2, 98%), bisphenol A (BPA, 99%), diethylstilbestrol (DES, 98%) hexoestrolum (HEX, 99%), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99%), terephthalic acid (H_2BDC, 98%), $NaNO_3$ (99.9%), ferrocenium hexafluorophosphate ($FcPF_6$) were from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. H_2BDC used for reactions in N_2 atmosphere was dried in a vacuum oven at 120 °C. Triethylamine hydrochloride (Et_3NHCl, 99.0%) was obtained from Sigma-Aldrich and recrystallized from absolute ethanol three times, then dried in a vacuum oven at 120 °C for over 12 h. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 99.0%) and tetrabutylammonium perchlorate (TBAP, 99.0%) were used as received from Fluka. Hydrofluoric acid (HF) (40.0%), N, N-dimethylformamide (DMF, 99.5%), Pt gauze (100 mesh, 99.9%) and wires (f = 0.404 mm, annealed, 99.9% metal basis, and f = 0.5 mm diameter, hard, 99.95% metal basis) were obtained from Sinopharm Chemical Reagent Co., Ltd., China. The stainless steel fibers (316 L, 100 μm O.D.) were obtained from an ironware factory in Ningbo.

The electrolyte solution was obtained by dissolving 38.8 g (100.2 mmol) $TBAPF_6$ (, in 1000 mL of DMF in a 1000 mL volumetric flask to form a 0.1 M solution and stored in a sealed bottle inside of an N_2-filled glovebox. The final polymerization solution contains: Et_3NHCl = 200 mM, $Zn(NO_3)_2{\cdot}6H_2O$ = 100 mM and H_2BDC = 50 mM.

Cyclic voltammetry (CV) and surface electrolysis experiments were carried out on an HI 650D Electrochemical Workstation (Shanghai, China), and using iron fiber as working electrode. All electrodeposition reactions were carried out on the stainless steel fibers. CVs were carried out in a standard three-electrode single-cell setups (stainless steel button working electrode (WE), Ag/Ag(cryptand)$^+$ reference electrode (RE), and Pt fiber counter electrode (CE)).