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Fabrication and application of zinc–zinc oxide nanosheets coating on an etched stainless steel wire as a selective solid-phase microextraction fiber

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ABSTRACT

A novel zinc–zinc oxide (Zn–ZnO) nanosheets coating was directly fabricated on an etched stainless steel wire substrate as solid-phase microextraction (SPME) fiber via previous electrodeposition of robust Zn coating. The scanning electron micrograph of the Zn–ZnO nanosheets coated fiber exhibits a flower-like nanostructure with high surface area. The SPME performance of as-fabricated fiber was investigated for the concentration and determination of polycyclic aromatic hydrocarbons, phthalates and ultraviolet (UV) filters coupled to high performance liquid chromatography with UV detection (HPLC-UV). It was found that the Zn–ZnO nanosheets coating exhibited high extraction capability, good selectivity and rapid mass transfer for some UV filters. The main parameters affecting extraction performance were investigated and optimized. Under the optimized conditions, the calibration graphs were linear over the range of 0.1–200 $\mu g\,L^{-1}$. The limits of detection of the proposed method were 0.052–0.084 $\mu g\,L^{-1}$ (S/N = 3). The single fiber repeatability varied from 5.18% to 7.56% and the fiber-to-fiber reproducibility ranged from 6.74% to 8.83% for the extraction of spiked water with 50 $\mu g\,L^{-1}$ UV filters ($n = 5$). The established SPME-HPLC-UV method was successfully applied to the selective concentration and sensitive determination of target UV filters from real environmental water samples with recoveries from 85.8% to 105% at the spiking level of 10 $\mu g\,L^{-1}$ and 30 $\mu g\,L^{-1}$. The relative standard deviations were below 9.7%.

1. Introduction

Solid-phase microextraction (SPME) has been extensively used as a powerful sample preparation technique in analysis of trace organic analytes since its introduction by Pawliszyn and co-workers in the early 1990s [1]. This technique is based on the partitioning of the organic analytes between the sample matrix and thin extraction coating deposited onto a fused silica fiber. As compared with traditional liquid–liquid extraction and solid-phase extraction, SPME is a simple, time-saving, sensitive and solvent-free technique by integrating sampling, extraction, concentration with sample introduction procedures for gas chromatography and high performance liquid chromatography (HPLC) in a single step [2]. Currently, commercially available coatings include polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene, carboxen, carbon nanotubes [3], carbowax and their composites. However, most of commercially available fibers are expensive and also suffer from some drawbacks such as low thermal and chemical stability, fragility, the stripping of coatings and easily swelling in organic solvents [4], which limit their widespread applications. Therefore, the development of fiber coatings with excellent physicochemical properties has attracted considerable research attention in the past two decades. The latest reports are on the use of synthesized nanomaterials as extraction coatings in the fabrication of SPME fibers [5]. These nanostructured coatings involve unique surface structures and properties which improves the extraction efficiency, selectivity and mass transfer of specified analytes. In particular, strong adhesion of uniform nanomaterial coatings onto metallic supports greatly improves the flexibility of the fibers and significantly prolongs the lifetime of the fibers. For these reasons, many efforts have directed to the development of special nanomaterials coated fibers with metal-based supports such as stainless steel (SS) wires [6–11], silver wire [12], platinum wires [13–15] and titanium wires [16–20]. These metal wire supported fibers

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are physically strong and can be handled with great convenience. Due to their quite different physicochemical properties from fused-silica fiber, there have been a great variety of preparation strategies for nanomaterial coatings with the metal wires as supporting substrates.

Zinc oxide (ZnO) is a promising material due to its good thermal stability, no toxicity, biocompatibility and easy preparation [21]. The first report about the application of ZnO-coated SPME fiber was presented for the extraction of thiophenol from water samples by Djozan and coworkers [22]. The results showed that the proposed fiber was selective for polar compounds. In recent years, ZnO nanorods and nanotubes have been prepared on fused silica fibers as SPME coatings based on hydrothermal synthesis method [23–26]. The as-prepared one-demensional ZnO coatings proved to exhibit satisfactory extraction capability for the selected organic compounds due to their high surface-to-volume ratio. However, the SPME fibers based on the fused silica support are easily broken and therefore their service life is limited. For this reason, ZnO nanorods based SPME coatings on SS wires were prepared using in situ hydrothermal growth method [27,28]. The prepared fibers showed excellent extraction efficiency for benzene homologues and aldehydes. So far, No applications except head space-SPME based on the gas adsorption properties of ZnO nanostructures have been reported for special ZnO-based structures. Thus, it is interesting and innovative work to fabricate a ZnO-based coating with alternative nanostructure and to find its potential applications in water analysis. Furthermore, developing simple, rapid and low-cost preparation strategies to fabricate ZnO nanostructures for SPME coatings is also desirable.

SS wire is inexpensive and was frequently used as a supporting substrate in preparing novel SPME fibers [6–11,27,28]. For the purpose of tight attachment of coating materials to the SS substrates, however, the SS wire often needed some additional pretreatments before subsequent coating procedure [29,30]. Surface etching is very promising for increasing the surface area of SS wire [31]. The etched SS wire provide a promising alternative substrate for further fabrication and strong adhesion of highly efficient coating materials to the SS substrate because it exhibits much larger surface area and better active sites [32–34]. Electrodeposition can offer a rigid control of coating thickness, uniformity and deposition rate for conductive coatings. This technique is especially attractive for further deposition onto the substrates with complex shapes [35]. In the present work, we presented a new approach to rapid and uniform electrodeposition of robust Zn coating on the surface of the etched SS wire using potentiostatic technique followed by its spontaneous oxidation in the atmosphere. This proposed procedure is simpler and more convenient than hydrothermal synthesis method. Extraction capability and selectivity of the Zn–ZnO nanosheets coated fiber were investigated for the concentration and determination of trace polycyclic aromatic hydrocarbons (PAHs), phthalates (PAEs) and ultraviolet (UV) filters coupled to HPLC with UV detection (HPLC-UV). Finally, this novel fiber was practically applied to the selective concentration and sensitive determination of trace target UV filters from different environmental water samples. Its SPME performance was also compared with that of commercial PDMS and PA fibers under the optimized conditions.

2. Experimental

2.1. Materials and reagents

Stainless steel wire (0.20 mm O.D.) was obtained from Gaoge (Shanghai, China). A polydimethylsiloxane (PDMS, 100 μm thickness) and polyacrylate (PA, 85 μm thickness) fibers were obtained from Supelco (Bellefonte, PA, USA). 0.45 μm micropore membrane of polyvinylidene fluoride was supplied by Xingya Purifying Material Factory (Shanghai, China). The HPLC-grade methanol was purchased from Yuwang Chemical Company (Shandong, China). Sodium chloride (NaCl) was obtained from Shanghai Hunter Fine Chemicals Ltd. (Shanghai, China). Certified individual standards of naphthalene (Nap), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu) and Pyrenees (Pye) were purchased from Aldrich (St. Louis, MO, USA). Certified individual standards of dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), di-n-octyl phthalate (DOP), di-(2-ethylhexyl) phthalate (DEHP), 2-hydroxy-4-methoxybenzophenone (BP-3), 2-ethylhexyl 4-methoxycinnamate (EHMC) and 2-ethylhexyl 4-(*N,N*-dimethylamino) benzoate (OD-PABA) were purchased from AccuStandard (New Haven, CT, USA). 2-Ethylhexyl salicylate (EHS) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). Stock standard solutions of 100 mg L^{-1} each compound were prepared in methanol and stored in amber bottles in the refrigerator at 4 °C, shielding from light. Working standard solutions were prepared by diluting the stock standard solution with ultrapure water to the required concentration to study extraction performance under different conditions. All other reagents were of analytical grade.

2.2. Apparatus

The chromatographic separation were performed on a Waters 600E multi-solvent delivery system (Milford, MA, USA) equipped with a Waters 2487 dual λ absorbance detector and a zorbax Eclipse Plus C18 column (150 mm × 4.6 mm, 5 μm, Agilent, USA). Data collection was obtained with a N2000 chromatographic workstation (Zhejiang University, China). Desorption was performed in a commercially available SPME-HPLC interface (Supelco, PA, USA) and sealed by polyether ether ketone septum which is tight enough to withstand pressure as high as 29.7 MPa. Ultrapure water was obtained from a Sudreli SDLA-B-X water purification system (Chongqing, China). Sample stirring and heating was carried out in a DF-101S water bath with magnetic stirrer and a temperature-controlled system (Changcheng, Zhengzhou, China). Electrodeposition of Zn coating was performed on a CHI832D electrochemical analyzer (Chenhua, Shanghai, China). The morphologies of the as-fabricated fiber were investigated by an Ultra Plus microscope (Zeiss, Oberkochen, Germany). The chemical compositions were determined by a energy dispersive X-ray spectrometer (EDS) attached to the SEM instrument.

2.3. Fabrication of Zn–ZnO coated fiber

A piece of SS wire (75 mm long) was cleaned with acetone and ultrapure water in an ultrasonic bath. Thereafter 2-cm segment of the SS wire was dipped into in hydrofluoric acid of 40% for chemical etching for 60 min at 40 °C. After the etched SS wire was thoroughly washed with methanol and ultrapure water in an ultrasonic bath, the etched segment was soaked into the electrolytic solution with different amounts of $ZnSO_4$ solution, 200 g L^{-1} KCl solution and 25 g L^{-1} boric acid according to modified procedure [36]. Electrodeposition of Zn coating was performed at applied potential of −1.2 V at 25 ± 1 °C in a three-electrode configuration with the SS wire as a working electrode, the platinum rod as a counter electrode and the saturated calomel electrode as a reference electrode. Subsequently the Zn coating electrodeposited on the etched SS wire was rinsed with ultrapure water and allowed spontaneous oxidation for the formation of compact and stable ZnO