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Selective solid-phase microextraction of ultraviolet filters in environmental water with oriented ZnO nanosheets coated nickel-titanium alloy fibers followed by high performance liquid chromatography with UV detection

Huiju Wang[a], Jiajian Du[a], Qi Zhen[a], Rong Zhang[a], Xuemei Wang[a,b], Xinzhen Du[a,b,*]

[a] College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China
[b] Key Lab of Bioelectrochemistry & Environmental Analysis of Gansu, Lanzhou 730070, China

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ABSTRACT

Uniform and dense ZnO nanosheets (ZnONSs) as a solid-phase microextraction (SPME) fiber coating were fabricated on the surface of nickel and titanium oxide composite nanosheets (NiO/TiO_2CNSs) which were in situ grown on the Nitinol (NiTi) wire in a hydrothermal procedure. The SEM micrographs illustrate that ZnONSs with the average thickness of 50 nm have been electrochemically grown on the NiTi fibers. The interconnected ZnONSs coating presents a porous nanostructure with large surface area. The as-fabricated fiber exhibits high extraction capability and excellent extraction selectivity for ultraviolet (UV) filters among the selected aromatic compounds. The main parameters affecting extraction performance were examined and optimized. Under the optimized conditions, the calibration curves were linear from 0.05 to 500 ng mL^{-1} with correlation coefficients above 0.999. The limits of detection (S/N = 3) ranged from 0.011 to 0.042 ng mL^{-1}, while the limits of quanitification (S/N = 10) were in the range of 0.037–0.14 ng mL^{-1}. Relative standard deviations (RSDs) for the single fiber repeatability were less than 7.4% (n = 5) and RSDs for the fiber-to-fiber reproducibility were below 8.2% (n = 5). The proposed method was successfully applied to the proconcentration and determination of trace UV filters in real water samples. Moreover, the ZnONSs coating can be fabricated in highly reproducible manner with long durability.

1. Introduction

Organic ultraviolet (UV) filters are a family of synthetic UV-absorbing compounds in which single or multiple aromatic structures are sometimes conjugated with carbon-carbon double bonds and/or carbonyl moieties, often with attached hydrophobic groups [1]. They are usually formulated in personal care products in order to protect human skin from solar radiation. Because of worldwide consumption of personal care products, a large amount of UV filters is directly or indirectly released into aquatic environment during bathing and washing activities through domestic wastewater [2]. Due to their lipophilic nature, some UV filters are able to penetrate skin barrier and lead to accumulative negative effect in tissues. Recently, many researches have demonstrated that some UV filters accumulated in biota could act as hormone disruptors, showing antiestrogenic, androgenic and antiandrogenic behavior [3]. Consequently, UV filters are recognized as emerging contaminants in environmental water. In most cases, however, they are present at trace or ultratrace levels in environmental water. It is difficult for their direct and accurate detection with conventional analytical instrument. Therefore, various extraction procedures were proposed for the preconcentration of UV filters prior to instrumental analysis [1].

Solid-phase microextraction (SPME) is an attractive alternative to conventional extraction or microextraction techniques [4], and has attracted great attention for its simple, fast, efficient and solventless features. Typically, a fiber-SPME assembly consists of a fiber substrate and its coating. In SPME, the target analytes are firstly extracted from the sample matrix to the fiber coating and then introduced into analytical instrument for their subsequent analysis. Therefore, the extraction of target analytes greatly depends on the nature of fiber coatings. Currently, several commercially available fused-silica SPME fibers are usually used with polymeric coatings such as polydimethylsiloxane (PDMS), polyacrylate (PA) and their composites. Some commercial fused-silica SPME fibers has been applied to the preconcentration and determination of UV filters from water [2,5–8]. In practical SPME applications, however, these fused silica-based fibers suffer from some

* Corresponding author at: College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China.
E-mail address: duxz@nwnu.edu.cn (X. Du).

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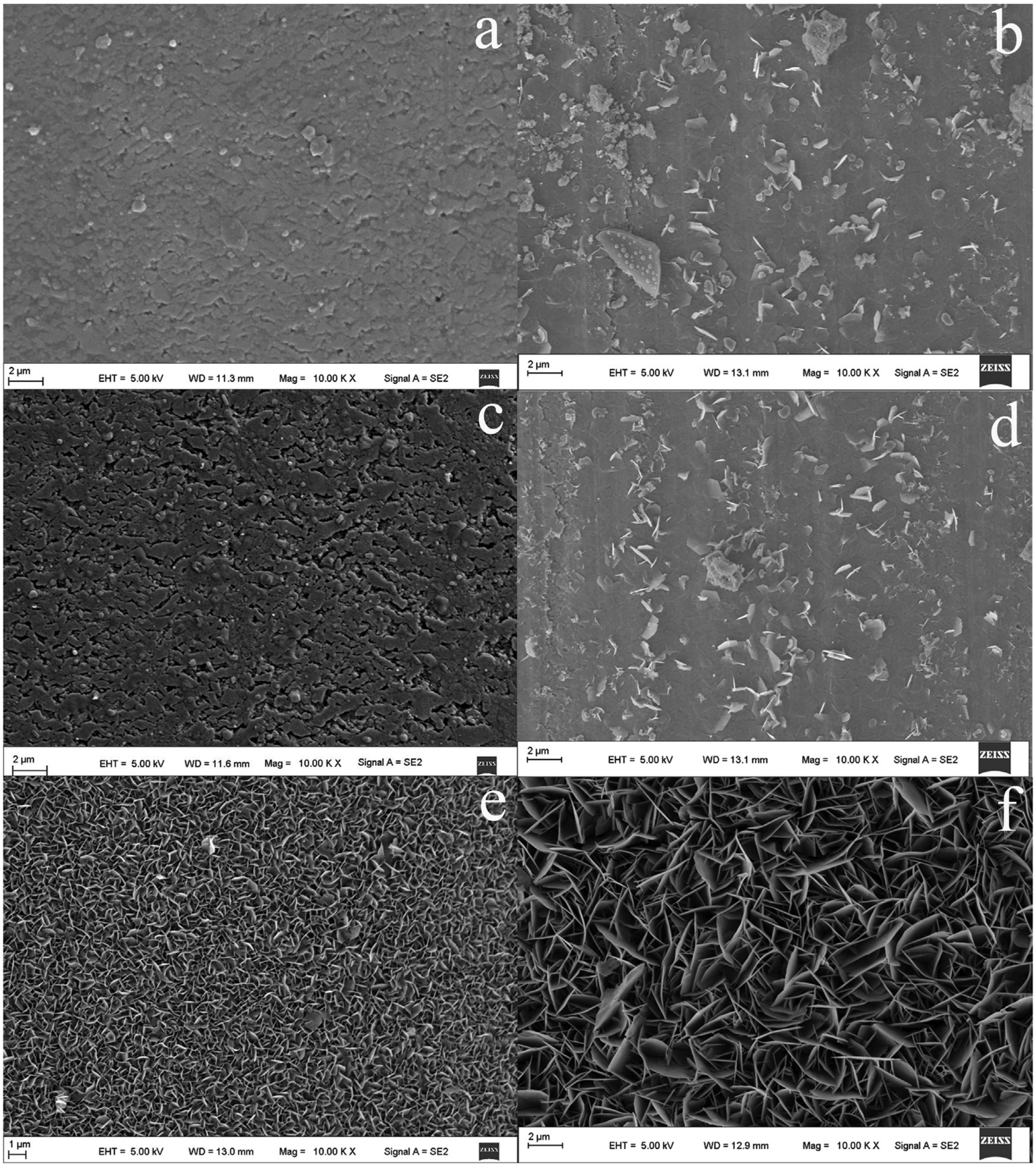

Fig. 1. SEM micrographs of the bare NiTi wire (a), the pretreated NiTi wire (c) and the hydrothermally treated NiTi wire (e) as well as corresponding ZnONSs grown on the bare NiTi wire (b), the pretreated NiTi wire (d) and the hydrothermally treated NiTi wire (f).

drawbacks such as easy breakage, poor extraction selectivity, relatively low thermal stability, possible swelling in organic solvents and short life span, which limit their widespread applications [4]. To overcome these shortcomings, enormous efforts have been devoted to the fabrication of novel metal-based fibers with high extraction efficiency, mechanical strength and chemical stability [9–14]. These unbreakable fibers presented high extraction capability and/or good extraction selectivity in some cases, which extends the SPME applications in the preconcentration and the determination of UV filters. In particular, nanostructured fiber coatings offer faster extraction kinetics at the same time.

ZnO is a promising metal oxide due to its excellent chemical and thermal stability, special electrical property, biocompatibility and easy preparation [15]. Some ZnO microstructures have shown great potential in SPME applications due to their high adsorptive capacity. So far, ZnO-based SPME coatings have been prepared and applied to headspace SPME of volatile or semi-volatile organic compounds [16–24]. Most of studies presented the preparation of one-dimensional ZnO nanorods on the fused-silica fibers [17,19–21] and the stainless steel wires [22–24] as SPME coatings via hydrothermal synthesis, and their high surface-to-volume ratios were proven to play a crucial role in the extraction of target analytes. Recently, the flower-like ZnO nanosheet coating was also fabricated on the stainless steel fiber for the selective preconcentration and the detection of typical UV filters in water samples [25]. However, no detailed descriptions were reported for the growth of oriented ZnO nanosheets (ZnONSs) on a nickel and titanium alloy fiber substrate.

Nitinol is a nearly equiatomic nickel and titanium alloy (NiTi) with shape memory effect, superelasticity, corrosion resistance and biocompatibility [26]. Consequently, a NiTi-based SPME fiber is a