Analytica Chimica Acta 900 (2015) 76–82

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Development and characterization of a nanodendritic silver-based solid-phase extraction sorbent for selective enrichment of endocrine-disrupting chemicals in water and milk samples

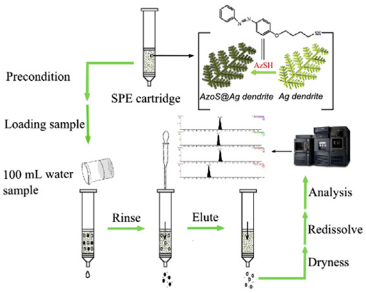
Yuanji Gao [1], Bing Xia [1], Jie Liu, Baocheng Ji, Fengwei Ma, Lisheng Ding, Bangjing Li, Yan Zhou [*]

Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, PR China

HIGHLIGHTS

- 4-[4-phenylazo-phenoxy] butyl-1-thiol (AzH) functioned nano-dendritic silver was prepared as SPE sorbent.
- The SPE sorbent exhibited excellent extraction performance to EDCs.
- The SPE sorbent was successfully applied to the analysis of EDCs in real water and milk samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form
6 October 2015
Accepted 17 October 2015
Available online 26 October 2015

Keywords:
Nanodendritic silver
Solid-phase extraction
Estrogens
Sample preparation

ABSTRACT

In this study, 4-[4-phenylazo-phenoxy] butyl-1-thiol (AzSH) functionalized nanodendritic silver (AzS@AgNDs) materials were prepared as a solid-phase extraction (SPE) sorbent for the selective extraction of estrogens. AzS@AgNDs possess an extremely large surface-to-volume ratio and a small average particle size. The performance of the material was evaluated by selective enrichment of hexestrol, diethylstilbestrol, dienestrol and bisphenol A in water and milk samples followed by rapid ultra-performance liquid chromatography–electrospray ionization mass spectrometry (UPLC–ESI–MS) analyses. The results exhibited that AzS@AgNDs had excellent adsorption capability for the targeted estrogens. The limits of detection of the four estrogens ranged from 0.1 to 5.0 pg/mL. The recoveries of the estrogens spiked into tap water were over the range of 83.6–105.3% with relative standard deviations of 2.8–6.0%. The results indicated the capability of this method for the rapid determination of estrogens in milk and other environmental water samples. In addition, this method would be useful for the determination of human exposure and health risk assessments trace level of endocrine-disrupting compounds (EDCs) in drinking water.

1. Introduction

Sample preparation is considered the most critical step in an overall analytical process because it has a multifarious role related to target analyte extraction, preconcentration and cleanup from co-

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[*] Corresponding author. Chengdu Institute of Biology, Chinese Academy of Sciences, No. 93 South Keyuan Road, Gaoxin Distinct, Chengdu 610041, PR China.
E-mail address: zhouyan@cib.ac.cn (Y. Zhou).

[1] These authors contributed equally.

http://dx.doi.org/10.1016/j.aca.2015.10.019

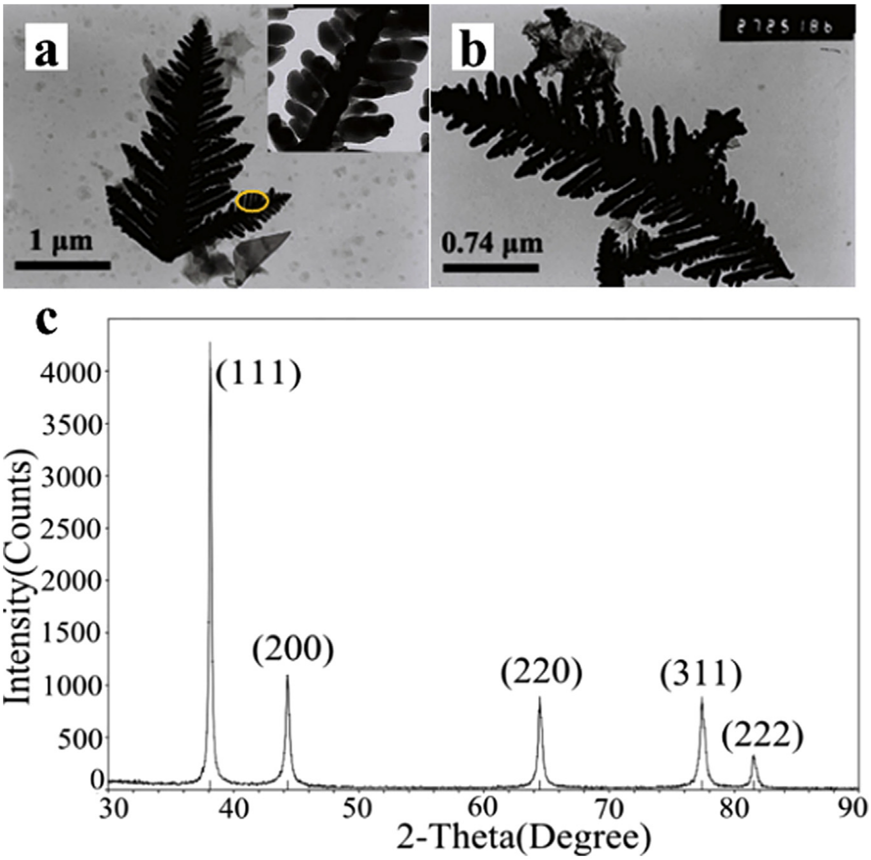

Fig. 1. TEM images of different Ag nanostructures obtained from the reaction: (a) and (b) dense, symmetricdendritic structure (~85%) and (c) XRD pattern of as-synthesized Ag nanodendrites. The insets of (a) provide higher resolution images of some characteristic nanostructures.

existing species [1]. For liquid sample analysis, to reach the required lower limits of detection (LODs), the most commonly used sample pretreatment is extraction of the analyte using solid-phase extraction (SPE) [2]. In most cases, matrix-related compounds can be co-extracted and can interfere in the analysis. To overcome this disadvantage, a selective and high-performance sorbent for SPE must be developed for purification prior to chromatographic analysis.

Dendritic materials have attracted increasing attention due to their unique physical and chemical features as well as their applications, such as targeted drug-delivery, macromolecular carriers, catalysis, sensors, light harvesting, surface engineering and biomimetic materials [3]. In addition to the obvious branched structures found in plants, dendrites can also be found in neurons, snowflakes, and in the microstructures of many commonly used materials. The properties of nanodendritic materials include their unique structure, large surface area, low density, rich surface chemistry, high catalytic activity, and low cost [4]. However, the potential applications of these nanodendritic materials as adsorbents in sample preparations have not yet been explored. Silver nanodendrites, which were formed using finely dispersed Zn microparticles as a reducing agent [5], might be used as a potential substrate for the preparation of an SPE sorbent.

Higher capacity, selectivity, affinity and sensitivity along with satisfactory extraction efficiency can be obtained using sorbents based on intermolecular interactions. Multiple intermolecular interactions between the target analytes and the adsorption centers of different types of sorbents have been used to achieve effective enrichment, and these interactions include hydrophobic interactions, π–π stacking, hydrogen bonding, electrostatic forces, van der Waals forces, ion exchange, as well as the molecular recognition mechanisms [6–8]. In this study, selective extraction of estrogens in water and milk samples was explored by means of molecular affinity between 4-[4-phenylazo-phenoxy] butyl-1-thiol (AzSH) on silver nanodendrites (AgNDs) and estrogens in water and milk due to their similar skeleton (C6–N=N(C=C)–C6 great π-conjugated system). In addition, AzSH possesses hydrogen bonding sites that can be used to selectively retain the target analytes, i.e. the hydroxyl groups of estrogens will form hydrogen bonds with the phenoxy oxygen *para* to phenylazo of AzSH.

Hexestrol (HEX), diethylstilbestrol (DES), dienestrol (DIS) and bisphenol A (BPA) are non-steroidal synthetic estrogens with estrogenic activity. Due to the anabolic effects of estrogens, they were illegally used as growth promoter in livestock breeding to increase the weight of animals by promoting protein synthesis and inhibiting fat aggregations. These estrogens could pose a threat to human health because they can be transferred to milk and other food products from treated animals as well as to the environment, causing adverse consequences associated with the consumption of food products or exposure to residues contaminating the environment. Much of the evidence has indicated that exposure to these synthetic endocrine-disrupting chemicals (EDCs) are physiologically active at picomole levels and may be of risk to human health due to their potential carcinogenic properties and other adverse effects [9–11]. Seventy-five percent of milk is produced from pregnant cows in the modern dairy industry. Therefore, the content of estrogens in commercial milk may have increased due to the illegal use of estrogens [12]. The control of their illegal use has