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Preparation of thiol- and amine-bifunctionalized hybrid monolithic column *via* "one-pot" and applications in speciation of inorganic arsenic

Ling-yu Zhao[a], Qing-yun Zhu[a], Li Mao[b], Yi-jun Chen[a], Hong-zhen Lian[a,*], Xin Hu[a,**]

[a] State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry & Chemical Engineering and Center of Materials Analysis, Nanjing University, Nanjing 210023, China

[b] MOE Key Laboratory of Modern Toxicology, School of Public Health, Nanjing Medical University, Nanjing 211166, China

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ABSTRACT

A thiol- and amine-bifunctionalized organic-inorganic hybrid monolithic column was prepared for the first time *via* one-pot co-condensation of 3-mercaptopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane and tetraethylorthosilicate, and utilized for separation and enrichment of inorganic arsenic species. Various parameters of solid phase microextraction (SPME) operation and analytical performance were also investigated systematically. Under the optimum condition, both As(III) and As(V) can be adsorbed over a wide pH range (3.0–8.0) and eluted in turn, in which 3% HNO_3 (v/v) was firstly used to selectively release As(V), and then 3% HNO_3 with 0.01 mol L^{-1} KIO_3 or 15% mercaptosuccinic acid (MSA) (m/v) to selectively release As(III). Meanwhile, the elution mechanism of As(III) and As(V) was elucidated comprehensively, and notably, the novel eluent, HNO_3 + MSA, was recommended for eluting As(III). Therefore, the thiol- and amine-bifunctionalized organic-inorganic hybrid monolithic column as an ideal SPME matrix for the speciation analysis of arsenic in environmental waters has the merits of facile preparation, low cost, high adsorption capacity and selective desorption. In addition, compared with thiol- and amine-bifunctionalized mesoporous silica, the bifunctional hybrid monolith based SPME protocol with less time and reagent consumption is promising to be applied not only to filed sampling but also to on-line analysis.

1. Introduction

In recent decades, human activities, such as mining and smelting processes, industrialization and urbanization, pesticide and fertilizer usage, waste incineration and wastewater irrigation, give rise to heavy metal contamination [1]. It is necessary to control the harmful effects of heavy metal ions through daily monitoring and removal technologies, due to their toxicity and tendency for bioaccumulation in plants, animals and human beings [2,3]. Over the years, scientists and engineers have been making a concerted effort to develop new materials and methods for the determination of trace elements and their species from aqueous solution. Solid phase microextraction (SPME), as a simple, solvent-saving, easy-to-automate, and portable sample preparation technique, has been applied to trace element speciation studies by selective preconcentration [4]. A variety of adsorbents, such as carbon, magnetic materials, mesoporous silica, and functionalized inorganic supports have been employed for the preconcentration of trace elements with satisfactory results [5]. In contrast to some other solid materials, significant attention has been paid to monolithic columns due to their uniform structure, controllable morphology, convective mass transfer and good adsorption capacity [6]. Moreover, monolithic columns have a wider range of applications, such as needle-SPME and on-line capillary solid phase microextraction (CME). Needle-SPME can be used for on-site processing of water samples without complex equipment to prevent the sample being contaminated during transport and storage, and on-line CME is of high sample throughput, low random error, and strong anti-interference ability [7]. Recently, Hu *et al.* have prepared a variety of monolithic columns for SPME-inductively coupled plasma mass spectrometer (ICP-MS) determination of trace elements. For instance, they prepared dual silica monoliths modified by mercapto and amino groups respectively in series for sequential speciation of inorganic arsenic (IAs) and selenium in natural waters [8], iminodiacetic acid modified glycidylmethacrylate (GMA)-*co*-trimethylolpropane trimethacrylate polymer monolithic column and mercaptosuccinic acid

* Correspondence to: School of Chemistry and Chemical Engineering and Center of Materials Analysis, Nanjing University, 163 Xianlin Avenue, Nanjing 210023, China.

** Corresponding authors.

E-mail addresses: hzlian@nju.edu.cn (H.-z. Lian), huxin@nju.edu.cn (X. Hu).

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(MSA) modified gold nanoparticles (Au NPs) functionalized GMA-*co*-ethylene dimethacrylate (EDMA) polymer monolithic column for trace rare earth elements analysis in human serum and urine samples [7,9], TiO_2 nanoparticles functionalized methacrylic acid-*co*-EDMA monolithic column for the analysis of Gd ion and Gd-based contrast agents in human urine [10], and so on. There are three kinds of monolithic columns, including organic polymer monolithic, inorganic silica monolithic and organic-inorganic hybrid monolithic columns. Because organic-inorganic hybrid monolithic columns have some merits such as good biocompatibility, large specific surface area and high mechanical stability [11], they were preferred in many fields, especially used for separation [12], among these three kinds of monolithic columns [13]. Functionalized hybrid monolithic columns were generally synthesized by post modification of inorganic monolithic columns or modified hybrid monolithic columns with active groups (vinyl and epoxy, *etc.)*, or by direct co-condensation of organosilane reagents with tetra-alkoxysilanes, either tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS), called "one-pot". Organic-inorganic hybrid monolith prepared *via* one-pot condensation process could make functional groups evenly distributed and preparing process simpler.

The contamination of groundwater, soils and drinking water with arsenic is a worldwide issue [14,15]. Arsenic can constitute a severe hazard to the whole ecosystem and public human health [16]. Arsenic is predominantly found as IAs species, As(III) and As(V), in environmental waters. Usually, As(III) is known to be the most toxic and more difficult to remove than As(V), due to reacting with -SH groups present in proteins [17,18]. It is not only important to remove As(III) and As(V), but also necessary for the quantitative determination of each arsenic species in daily monitoring [4,5]. Because two oxidation states of arsenic in environmental waters, As(III) and As(V), have different properties, the functional groups as specific ligands for each species are not the same. For example, amine has a strong affinity to As(V) [4,19], but thiol to As(III) [20–22]. It is difficult to simultaneously adsorb them with thiol- or amine-monofunctionalized monolithic columns. To date, the most commonly used method of evaluating both IAs species is to selectively adsorb As(III)/As(V) firstly, then calculate the other species by subtraction from the total IAs, or extract the sample again after adjusting the sample pH [23,24] or transferring the other one to As(III)/As(V) by pre-reduction/pre-oxidation operation [25–27]. However, these operations are time-consuming, of operational complexity, and may cause labile species change and introduce interferences.

Currently, it has become a trend to use a material integrating multiple functional groups to accommodate the enrichment and separation of different components. Feng *et al.* improved hybrid monolithic columns with octyl (C_8) and sulfo groups for capillary electrochromatography (CEC) to analyze theophylline and caffeine in beverage, and developed a solid phase extraction (SPE)-nano-LC-MS method with C_8- and $PO(OH)_2$-bifunctionalized hybrid monolith to determine gibberellins [28,29]. Yao *et al.* prepared a sulfo/vinyl biphasic hybrid monolithic column applying to preconcentration of low abundance peptides, and a n-octadecanethiol and 3-mercapto-1-propane-sulfonate modified hybrid monolithic column for CEC to separate organic molecules [30,31]. Zhang *et al.* decorated 4-mercaptophenylboronic acid and 2-mercaptoethylamine on the Au NPs modified GMA-*co*-poly(ethylene glycol) diacrylate monolith to prepare a hydrophilic boronate affinity monolithic column for glycoprotein enrichment [32]. Jiang *et al.* synthesized a mixed phospholipid (12-methacryloyl dodecylphosphocholine and 12-methacryloyl dodecylphosphoserine) functionalized monolithic column for early screening of drug induced phospholipidosis risk [33]. Wang *et al.* proposed a boronate-functionalized graphene-coupled poly(guanidinium ionic liquid) interface-free two-dimensional monolithic material for the separation of multiple types of glycoproteins [34]. The multifunctional materials that have been reported are mainly for organic pollutants and biomolecules in environmental and biological samples, however, relatively rare for elemental speciation analysis. Eroğlu *et al.* synthesized thiol- and amine-bifunctionalized silica by post-modification for speciation/sorption of IAs [23]. In our previous work, a homemade syringe-based SPE device with thiol- and amine-bifunctionalized mesoporous silica was developed and used to simultaneously separate and pre-concentrate As (III) and As(V) in a single run without changing any sample conditions [5].

As far as we know, there have been no reports relating multi-functional hybrid monolithic columns, especially synthesized by "one-pot", for elemental speciation analysis up to date. Although the syringe SPE by functionalized mesoporous silica is generally inferior to the needle-SPME based on the monolithic column with the same functional groups in aspect of time and reagent consumption, there are many similarities between mesoporous silica and hybrid monolithic column, and the synthesis conditions and characterization results of the functionalized mesoporous silica can provide inspiring reference for the preparation of the monolithic column decorated by the same functional groups [22]. In view of the advantages of hybrid monolithic column, in this paper, a novel thiol- and amine-bifunctionalized hybrid monolithic column was prepared *via* one-pot process for separation and enrichment of speciation of IAs by needle-SPME. The influences of various parameters of SPME and the types of eluents for As(III) were also investigated. Then the bifunctional hybrid monolithic columns as needle SPME materials were used for the simultaneous speciation analysis of As(III) and As(V) in environmental waters without changing sample conditions or transforming arsenic species during whole process.

2. Materials and methods

2.1. Reagents and materials

Cetyltrimethylammonium bromide (CTAB) was purchased from TCI (Tokyo, Japan). 3-Mercaptopropyltrimethoxysilane (MPTMS) and tetraethylorthosilicate (TEOS) were purchased from Alfa Aesar (Tianjin, China), and N-(2-aminoethyl)-3-aminopropyltriethoxysilane (AEAPTES) was purchased from Ourchem (Shanghai, China). Mercapto acetic acid (TGA) and mercaptosuccinic acid (MSA) were purchased from J&K (Shanghai, China). HNO_3 was of guaranteed reagent grade and obtained from Merck (Zurich, Switzerland). All other chemicals were at least of analytical grade and used without further purification. Pure water (18.25 MΩ cm) obtained from a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout the experiment.

Stock standard solutions of As(III) and As(V) (1000.0 mg L^{-1}) were prepared by respectively dissolving appropriate amounts of Na_3AsO_3 and As_2O_5 (both of analytical grade, purchased from Johnson Matthey, UK) in water. Lower concentration standard solutions were prepared daily by appropriate dilutions from their stock solutions.

2.2. Preparation of thiol- and amine-bifunctionalized hybrid monolithic capillary column

The fused-silica capillary (Reafine Chromatography Ltd., Hebei, China) with 530 μm i.d. and 690 μm o.d. was used to prepare the monolithic capillary column. Prior to preparation, the capillaries were washed at ambient temperature with 1.5 mol L^{-1} NaOH (10 h), water (30 min), 1.5 mol L^{-1} HCl (10 h), water (30 min), and methanol (30 min) successively to activate the silanol groups on the wall. Then, the capillaries were dried under nitrogen flow at 160 °C for 3 h.

The thiol- and amine-bifunctionalized monolithic gels were prepared from a solution containing CTAB, ethanol, water, MPTMS, AEAPTES and TEOS as illustrated in Scheme 1. The optimal preparation conditions were as follows: 250 μL ethanol, 100 μL water and 22.2 mg CTAB were mixed together in a 1.5 mL Eppendorf vial. Subsequently, 160 μL TEOS, 20 μL AEAPTES and 20 μL MPTMS were added into the above mixture followed by vortexing at room temperature for 30 s and ultrasonicating at 0 °C for 30 s. The resulting sol was then filled into the pretreated capillary with a certain length by a syringe. After being