



Preparation and analytical application of novel thiol-functionalized solid extraction matrices: From mesoporous silica to hybrid monolithic capillary column

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ABSTRACT

A comprehensively comparative study of thiol-functionalized mesoporous silica and organic-inorganic hybrid monolithic column was reported, aiming at the separation and enrichment of inorganic arsenic. Thiol-functionalized mesoporous silica was synthesized based on the one-step co-condensation method. At the same time, a novel thiol-functionalized organic-inorganic hybrid monolithic column was synthesized using an unconventional ternary weak basic solvent system *via* one-step sol-gel process. The approach to prepare monolithic column through mild condition remarkably improved delamination phenomenon of thiol-functionalized hybrid monolithic column easily caused by conventional methods. As(III) can be selectively uptaken by the hybrid monolithic column and homemade syringe-based solid phase extraction device containing mesoporous silica through chelation in a wide range of pH, while As(V) cannot, and then the captured As(III) was eluted by 3% HNO₃ (v/v) with 0.01 mol L⁻¹ KIO₃. Under the optimized conditions, the extraction recoveries were 91–102% and 93–103% for mesoporous silica and monolithic column, respectively. Although both two materials were ideal solid matrices for the removal and speciation analysis of As(III) in environmental waters, the monolith-based solid phase microextraction protocol was more fast and reagent-saving than the other, which ended monolithic columns with more application prospects for trace elemental analysis and speciation. Even so, the exploration of mesoporous silica could efficiently pilot the synthesis of monolithic columns.

1. Introduction

Trace metals exhibit widely different toxicities depending on their elemental species in the environment [1]. Arsenic, as a kind of main contaminate element of groundwater, soils and drinking water, derived from natural weathering of rocks, combustion of fossil fuel, the usage of arsenic pesticide and so on, has attracted major attention in large regions in the world [2,3]. The long-term exposure to arsenic-contaminated environment can cause many diseases, like dermatosis and the cancers of nasal passages and viscus [4]. The limited maximum concentration of arsenic stipulated by the World Health Organization is 10 µg L⁻¹ in drinking water [5]. Arsenic exists in two predominant inorganic species, arsenite As(III) (H₂AsO₃⁻, HAsO₃²⁻ and AsO₃³⁻) and

arsenate As(V) (H₂AsO₄⁻, HAsO₄²⁻ and AsO₄³⁻). As(III) is usually the dominant arsenic in environmental water. Because As(III) could react with mercapto group present in proteins, As(III) is usually more toxic and difficult to remove than As(V) [4,6,7]. Thus, separation and determination of As(III) and As(V) for the speciation analysis of arsenic is very necessary.

Solid phase microextraction (SPME), as a typical successful miniaturized sorbent-phase extraction technique, has been applied to element speciation studies by selective preconcentration, with a series of advantages such as high sensitivity, low sample requirement, low solvent consumption, simplicity, and easy automation [8]. Commonly used solid phase extraction (SPE) materials include polymer particles, biomass, carbon, zeolites, functionalized inorganic supports, mesoporous

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silica, and capillary monolithic columns [9]. In contrast to some other solid materials, mesoporous silica and monolithic column as SPE/SPME matrices have attracted significant attention. Mesoporous silica has good dispersibility and controllable morphology, and shows a large adsorption capacity due to its large specific surface area [10]. Various functionalized mesoporous silicas with thiol, amine, phosphonate and so on, have been used for SPE to analyze heavy metals [10–13]. A small problem is that mesoporous material for SPE needs to achieve solid-liquid separation by centrifugation, which is a little tedious. To avoid this problem, we previously reported a homemade syringe-based SPE device containing thiol and amine-bifunctionalized mesoporous silica for the simultaneous uptake of As(III) and As(V) [9].

Capillary monolithic columns have been widely used for needle-SPME and on-line capillary solid phase microextraction (CME), because of their unique advantages, like uniform structure, controllable morphology, convective mass transfer and easy to automate [8]. Although the application of monolithic materials shows a great success in the area of organic and biological substances, it should be stressed that only a few applications have been reported on the analysis of trace elements and their speciation. For instance, Hu et al. proposed some methods based on capillary monolithic columns for CME-inductively coupled plasma mass spectrometer (ICP-MS) determination of trace elements. They connected two silica monolithic columns in series, which were respectively modified by amine and mercapto groups, to sequentially separate inorganic arsenic and selenium in natural water [14]. They also developed two kinds of functionalized polymer monolithic columns to analyze trace rare earth elements in human serum and urine samples [15,16], and proposed a TiO₂ NPs modified polymer monolithic column for the analysis of Gd³⁺ and Gd-diethylene triamine pentaacetic acid in human urine [17].

In comparison with classical inorganic silica and organic polymer monolithic columns, organic-inorganic hybrid monolithic columns prepared by a sol-gel reaction were preferred in some fields because of some advantages, such as large specific surface area, good biocompatibility and high mechanical stability [8,18]. In view of the special interaction of As(III) with mercapto groups, it will be a good choice to analyze As(III) using thiol-functionalized hybrid monolithic columns.

During the sol-gel reaction, silane reagents tend to hydrolyze under acidic conditions and polymerize under alkaline conditions. If the pH of pre-polymerization solution does not vary during the sol-gel process and silane reagents could hydrolyze and polymerize at the same time, this process would be called “one-step”. However, the presence of mercapto groups makes the solution acidic, which is difficult for silane reagents to polymerize. In the previous works, mercapto groups were generally introduced by post-modifying mercapto groups to the surface of prepared silica monoliths or hybrid monoliths with other active groups (such as vinyl) [14,19–21]. Mercapto groups only and unevenly exist on the surface of monoliths, and monolithic columns were hard to repeat through this kind of method. The other main method is to hydrolyze the pre-polymerization solution firstly under acidic or neutral condition at low temperature and then polymerize after adding basic solution inside [22–24]. Unfortunately, the polymerization process takes place in a very short period of time once the base is added, and there is not enough time to react with the inner wall of capillary, which easily makes monoliths not anchor tightly and requires high operator's skill. Here, we pay attention to preparation of an easy-to-prepared thiol-functionalized organic-inorganic hybrid monolithic column via “one-step”.

In fact, there are many similarities between mesoporous silica and hybrid monolithic column. Contrasting these two materials, same silane reagents were used in the synthesis process depending on the similar reaction mechanism. The difference is that mesoporous silica has more ways to characterize the framework structure and the successful introduction of functional groups because they are synthesized *in vitro*, however, the monolithic column materials need to be characterized after removal from the capillary, during which the backbone structure

would be destroyed, and some characterization data are not accurate enough. The characterization results and synthesis conditions of functionalized mesoporous silica can provide inspiring reference for the preparation of organic-inorganic hybrid monolithic columns decorated by the same functional groups.

In this present work, we synthesized a thiol-functionalized hybrid monolithic column under unconventional ternary weak basic solvent system by a one-step procedure. Meanwhile, thiol-functionalized mesoporous silica was also prepared and used to fabricate a homemade syringe-based SPE device. Both the syringe-based SPE devices and monolithic column could selectively adsorb As(III) and therefore be used for separating and enriching As(III) in environmental water excluding As(V) interference, while the needle-SPME by thiol-functionalized hybrid monolithic column is better comparing with syringe-based SPE device. To the best of our knowledge, this is the first time to contrast the preparation and analytical application of mesoporous silica and hybrid monolithic column in one work.

2. Experimental section

2.1. Reagents and solutions

Cetyltrimethylammonium bromide (CTAB) was brought from TCI (Tokyo, Japan). Tetraethylorthosilicate (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) were purchased from Alfa Aesar (Tianjin, China). Sodium hydroxide (NaOH) was got from Nanjing Chemical Reagent Co. Ltd. Hydrogen nitrate (HNO₃) was of guaranteed reagent grade and obtained from Merck (Zurich, Switzerland). Isopropanol (IPA) and ethanol were purchased from Nanjing WanQing Chemical Glassware & Instrument Co. Ltd. Other chemicals were of analytical reagent grade and used without further purification. Deionized water (DIW) of 18.25 MΩ cm collected from a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout the experiment.

1000.0 mg L⁻¹ stock solutions of inorganic As(III) and As(V), respectively, were prepared by dissolving Na₃AsO₃ and As₂O₅ (both of analytical reagent grade, purchased from Johnson Matthey, UK) in DIW. Lower concentration solutions were prepared daily by diluting the stock solutions with DIW.

Rain water was contained in our lab in the downtown campus located in Gulou District, Nanjing. River water was collected from Qinhuai River in Gulou District, Nanjing. Each environment water was filtered through a 0.45 μm cellulose acetate membrane before used.

2.2. Preparation of thiol-functionalized mesoporous silica and syringe-based SPE device

The thiol-functionalized mesoporous silica was prepared as followed (Scheme 1). In detail, 0.5 g of surfactant, CTAB, as the template, and 3.5 mL NaOH (1.0 mol L⁻¹) were dissolved in 120 mL DIW in a 250 mL 3-neck round bottom flask. The reaction system was stirred for 20 min at 80 °C. After the solution became clarified, a mixture of TEOS and MPTMS was dropped in using a pump (Baoding Longer, Model BT100) as impulse. After 10 min, fine white solid materials were obtained. The reaction mixture was stirred for another 2 h at 300 rpm under a nitrogen atmosphere. The resulting white powders were isolated by filtration under reduced pressure, washed with DIW (3 × 5 mL) and ethanol (3 × 5 mL), and then dried overnight at room temperature. The dried solid was added into a solution of ethanol and 1 mol L⁻¹ HCl (1 g of synthesized material in 100 mL ethanol with 0.5 mL HCl) refluxing for 48 h at 80 °C to remove CTAB. After washed with DIW until neutral, the material was rinsed with ethanol and dried overnight at room temperature. In order to evaluate the influence of the molar ratio of MPTMS to silane reagents in the reaction system, the molar composition of the reaction mixture was set to (1-x) TEOS: x MPTMS: 0.11 CTAB: 0.28 NaOH: 532H₂O. Then, five thiol-functionalized mesoporous silica products, which were labeled as TFMS1 to

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