



## Preparation, characterization and analytical application of a hybrid organic–inorganic silica-based monolith

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### ARTICLE INFO

#### Article history:

Received 16 January 2008

Received in revised form 22 April 2008

Accepted 25 April 2008

Available online 3 May 2008

#### Keywords:

Silica monolith

Hybrid material

Mercapto

Sol–gel

In-tube microextraction

### ABSTRACT

In the present study, a mercapto groups-incorporated hybrid silica-based monolith, which consists of a continuous porous silica backbone, was successfully synthesized by sol–gel technology. The hybrid silica monolith was characterized by various techniques, such as elemental analysis, scanning electron microscopy, diffused infrared spectroscopy and low temperature nitrogen desorption/adsorption measurements. The results showed that the monolith contains high sulfur content (up to 3.05%) with a hierarchical porous structure (throughpores and mesopores) and large specific surface area ( $467 \text{ m}^2/\text{g}$ ). Due to the favorable chemical reactivity of mercapto pendant moieties, the hybrid monolith can be facilely derivatized to yield various functional groups. In this study, they were oxidized by hydrogen peroxide (30%, w/w) to produce sulfonic acid groups, which exhibited excellent cation-exchange capability. The application of this material is demonstrated by in-tube microextraction of anaesthetics followed by capillary electrophoretic separation. The monolith can be effectively applied to purify and enrich the target analytes in human urine.

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### 1. Introduction

Generally, hybrid materials are referred to as materials comprising two or more integrating components which combine at the molecular or nanometer level. One obvious property of hybrid materials is that they can be specially tailored to give desirable properties or to suppress undesirable ones for wide-ranging applications. They have been broadly used in analytical chemistry as sensors, stationary phases for high performance liquid chromatography (HPLC) and extraction sorbents [1].

Monolithic materials have been attracting attention recently as alternative stationary phases for HPLC, capillary electrochromatography (CEC) and as extraction sorbents, due to their fast dynamic transport, elimination of need for the frits (necessary for particle-packed columns) and their satisfactory loading capacity that is superior to that of open tubular columns [2]. Basically, monolithic materials are grouped into two matrices: polymer- and silica-based. Since they can circumvent disadvantages associated with polymeric ones, such as swelling and shrinking under the influence of temperature and/or organic solvents, silica materials possess huge potential for applications in various fields [3], such as catalysis at high temperature in various organic solvents.

A silica monolith is generally used after modification with desirable functional groups via traditional chemical bonding methods. However, this type of chemically bonded silica-based materials suffer from several defects, multi-step synthesis and probable low loading of the functional groups. Moreover, organic functional groups can be evenly distributed in the structure of the inorganic matrix, which facilitates the achievement of excellent performance in applications [4,5]. Recently, there have been reports of hybrid silica-based monoliths being prepared by sol–gel technology. The materials have been especially investigated as CEC stationary phases containing different groups, e.g. allyl [6], octadecyl [7], phenyl [8], octyl [9] and amino [10]. However, this approach is limited because it requires careful control of synthesis conditions to obtain the defined monolithic configuration in the presence of dissimilar precursors. This implies that the synthesis conditions for hybrid monolithic structures containing different functionalities have to be optimized individually [11]. Hence, its development has been inhibited when compared to that of chemically bonded materials.

In this study, we incorporated mercapto groups into the silica precursor by sol–gel technology, forming the organic–inorganic hybrid monolith. The mercapto organic moiety was chosen, because it can be conveniently derivatized into diverse functionalities. There have been some reports about mercapto-modified monoliths. Preinerstorfer et al. [12] studied the transformation of 2,3-epoxypropyl groups of poly(glycidyl methacrylate-co-ethylene

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dimethacrylate) monolith to give thiol groups. Xie et al. modified a silica monolith with 3-mercaptopropyltrimethoxysilane (MPTS) to yield thiol groups. A two-step process was reported that included the synthesis of the silica monolith and subsequent modification by a chemically bonding method [13]. The aim of the present study is to synthesize the mercapto groups-incorporated silica-based hybrid monolith in a single step by sol-gel technology. Unlike the aforementioned previous studies, the present approach does not involve surface modification; it concerns the preparation of a monolith from the outset. Synthesis conditions, including solvent category, poly(ethylene glycol) (PEG) content, reaction temperature, reactant ratios and pH, were studied in detail. Subsequently, the resulting materials were characterized by elemental analysis (EA), scanning electron microscopy (SEM), diffused infrared spectroscopy (IR) and low-temperature nitrogen desorption/adsorption measurements. One example of its application was demonstrated by oxidization using hydrogen peroxide ( $H_2O_2$ ) to yield sulfonic acid groups, which was then applied to the in-tube microextraction of anaesthetics, and further studied by using it for the extraction of analytes in spiked human urine, followed by capillary electrophoretic (CE) separation.

## 2. Experimental

### 2.1. Regents and materials

Fused-silica capillaries of  $250\ \mu\text{m}$  i.d.  $\times$   $365\ \mu\text{m}$  o.d. were obtained from Hebei Yongnian Optical Fiber Factory (Hebei, China), while  $50\ \mu\text{m}$ -i.d. bare fused-silica capillaries were purchased from Polymicro Technologies (Phoenix, AZ, USA). Tetramethoxysilane (TMOS) and MPTS were obtained from the Chemical Factory of Wuhan University (Wuhan, China).  $H_2O_2$  (30%, w/w) and PEG (Mw = 10,000) were purchased from Shanghai General Chemical Reagent Factory (Shanghai, China). Anaesthetics procaine, lidocaine, tetracaine and bupivacaine were purchased from Aldrich (Milwaukee, WI, USA). HPLC-grade methanol was obtained from Fisher (Loughborough, UK). Ammonia ( $NH_3 \cdot H_2O$ ) and hydrochloric acid (HCl) were purchased from Merck (Darmstadt, Germany). Ultrapure water was produced on a Nanopure (Barnstead, Dubuque, IA, USA) water purification system.

### 2.2. Apparatus

The CE experiments were performed on a HP<sup>3D</sup> CE system (Hewlett-Packard, Waldbronn, Germany) equipped with on-column diode array detection (DAD) system. A 51-cm-long,  $50\ \mu\text{m}$ -i.d. bare fused-silica capillary having a detector window at 42.3 cm from the inlet was used for separation. Before use, the capillary was pretreated, in succession, with 1 M NaOH for 2 h, water for 10 min, 1 M HCl for 2 h and then water for 10 min. Data were collected by HP<sup>3D</sup> ChemStation software (Hewlett-Packard). The limits of detection (LODs) were calculated according to peak height and at a signal-to-noise ratio of 3. The detection wavelength was 200 nm. All the experiments were performed at least in triplicate.

The pH of the buffer was measured using a pH meter, calibrated with aqueous standard buffer solutions. Before use, the buffer was degassed in an ultrasonic bath (Midmark, Versailles, OH, USA) for 5 min and filtered through a membrane of  $0.25\text{-}\mu\text{m}$  pore size.

CE separations of the tested four analytes were carried out in phosphate buffer at a pH of 2.4. A positive voltage of 15 kV was used for separation.

A Harvard Apparatus (Holliston, MA, USA) PHD 2000 syringe pump was used for in-tube microextraction.

### 2.3. Preparation of the hybrid monolith

Hybrid monoliths were prepared by a sol-gel process. Typically, 0.1 g of PEG was dissolved in 1.0 mL of water first, and then 1.0 mL of TMOS, 0.3 mL of MPTS and 2 mL of methanol were added. After being vigorously stirred at 273 K for 30 min, ammonia was introduced. Twenty minutes later, the sol obtained was transferred into a 3-mL polypropylene vial. To prepare the in-tube microextraction column, the sol was pumped into a fused capillary ( $15\ \text{cm} \times 250\ \mu\text{m}$  i.d., final monolith length of 15 cm), and sealed at both ends by silicone rubber. Thereafter, the capillaries filled with the sol and the residue sol in the polypropylene tube were placed in an oven at 313 K for reaction. Twenty hours later, gelation took place, leading to the formation of the wet silica gels. After being kept in situ at room temperature for 2 days, the monolith in the capillary was connected to a syringe pump and was washed for 24 h, sequentially, with water and methanol at a flow rate of 2.5 mL/h; while the sol in the polypropylene tube was immersed in water for 12 h (with a change of fresh water every 2 h), and then in methanol for 12 h (with a change of this solvent every 2 h). Finally, the materials were dried at 313 K for another 3 days. The hybrid monoliths thus obtained were used for the following characterization and application.

### 2.4. Characterization of the hybrid silica monolith

A JEOL (Tokyo, Japan) JSM-5200 scanning electron microscope was used for SEM observations. The monolith was fixed on the stub by a double-sided sticky tape and then coated with platinum by a JFC-1600 (JEOL) Auto fine coater for 50 s. Surface area and pore size analysis were carried out on a Coulter (Miami, FL, USA) SA 3100 Plus surface area and pore size analyzer. EA was carried out on PerkinElmer (Shelton, CT, USA) Model PE 2400 with a CHN combustion tube. Diffused IR was performed on an Avatar-360 FTIR instrument (Thermo Nicolet, Madison, WI, USA).

### 2.5. Oxidization of hybrid silica monolith

For oxidization, the hybrid monolith was flushed with  $H_2O_2$  (30%, w/w) for 24 h at room temperature and then washed with plenty of water to remove the excess  $H_2O_2$ .

### 2.6. Sample preparation

Stock solutions (1 mg/mL of each analyte) were prepared separately in methanol. Water samples were prepared by spiking ultrapure water with analytes at a known concentration ( $500\ \mu\text{g/L}$ ) to study extraction performance under different conditions. Urine sample was collected from volunteer. It was first filtered through a membrane of  $0.25\text{-}\mu\text{m}$  pore size. Afterwards, the filtrate was directly spiked with four anaesthetics, and then the pH was adjusted to three with HCl.

### 2.7. Application: in-tube microextraction process

The oxidized hybrid monolith fabricated in the capillary was directly used for in-tube microextraction. The experiment was carried out as follows. (1) Preconditioning: the monolith was initially flushed with methanol and water in that order for 3 min, respectively; (2) sample loading: the sample solution was then pumped through the capillary for a prescribed time (800 s) at a certain flow rate (1.5 mL/h); (3) washing: the monolith was washed with water for 3 min to remove any possible impurity; (4) elution: the elution solution (0.25% ammonia solution with 80% methanol) was pumped through the monolith at a specified flow rate (0.5 mL/h) for a prescribed time (600 s) and was collected into a  $200\ \mu\text{L}$ -capacity

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