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# A highly ordered chiral inorganic mesoporous material used as stationary phase for high-resolution gas chromatographic separations<sup>☆</sup>

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## ABSTRACT

A highly ordered chiral mesoporous silica-coated capillary column has been used for high-resolution gas chromatographic separations. The column has excellent selectivity, not only for the separation of isomers, polycyclic aromatic hydrocarbons, linear alkanes, long chain alkanes, Grob's test mixture and aromatic hydrocarbons, but also for the resolution of different classes of chiral compounds. Additionally, the column exhibits high column efficiency, excellent temperature resistance, and analysis times are short. This is the first report of a highly ordered chiral inorganic mesoporous silica used in separation science.

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## 1. Introduction

Since the discovery of the first ordered mesoporous silica (OMS) material in 1992 [1,2], such materials have been exploited in many areas of materials science because of their advantageous properties that include adjustable pore diameter, high specific surface area, and pore capacity [3–9]. Similarly, an important type of mesoporous material, chiral mesoporous silica has also attracted much attention. It is well known that chirality is often present in organic materials, but chirality of inorganic mesoporous material is rare. To date, chiral OMS has been reported as a liquid chromatography stationary phase [10], but the chiral OMS is an organic-inorganic hybrid material composed of organic chiral molecules immobilized on inorganic mesoporous materials. The chirality of OMS is derived from the grafting of chiral organic molecules, rather than the pore structure of the material itself or the backbone structure. The material, in particular, is not resistant to high temperatures. It has been found that chiral inorganic mesoporous materials can be obtained using a “template” pathway on the basis of soft chemistry. For

example, HMS (Hexagonal Mesoporous Silica) [11], SBA (Santa Barbara Amorphous) [12,13], KIT (Korea Advanced Institute of Science and Technology) [14], FDU (Fudan University) [15,16] and others have been synthesized by using nonionic and cationic surfactants as the templates. Nonetheless, only lamellar phases or disordered mesoporous materials have generally been obtained [17].

In 2004, highly ordered chiral mesoporous silica (HOCMS) [18], a novel inorganic porous material having a twisted hexagonal rod-like morphology and highly ordered helical nano-sized channels, was first reported by Che et al. The chirality of HOCMS results from interaction of a chiral anionic surfactant (C<sub>14</sub>-L-AlaA) with a co-structure-directing agent (CSDA). Mesoporous materials have been used in catalysis [19], adsorption [20], drug delivery [21], membranes [22], tissue engineering [23] and sensing [24]. HOCMS could also serve as a novel separation media for gas chromatography (GC) because of its helical mesostructure and high thermal stability. At present, there are many GC chiral stationary phases, such as cyclodextrin and its derivatives [25], chiral metal organic frameworks [26], chiral ionic liquids [27], and chiral porous organic cages [28]. However, to the best of our knowledge, the maximum usable temperature of the stationary phase is limited to 230–250 °C, and they are often difficult to use at high temperature. It is therefore necessary to explore a capillary GC column with high selectivity and increase the usable temperature range to expand the variety of racemates that can be separated. Recently, chiral nematic

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mesoporous silica (CNMS) was synthesized by the method of chiral liquid-crystal assembly, and has been used as a stationary phase for GC by our group [29]. This capillary column showed good chiral recognition ability of ten chiral compounds and, notably, could endure temperatures of up to 350 °C. This research provides a new avenue for development of chiral capillary columns with high separation efficiency that can be used at high temperatures in GC.

Herein we report an HOCMS-coated open tubular column for high-resolution GC separation of compounds. The stationary phase was synthesized using the structure-directing method, which uses hard rather than soft materials. Such chiral materials have a clear advantage of physical strength compared with chiral liquid-crystal assemblies, yielding a permanent chiral space. Ultimately, it combines the advantages of high thermal and chemical stability, high specific surface area and pore capacity, adjustable pore diameters, unique mesostructure and morphology with the inherent chirality of HOCMS, some isomers, polycyclic aromatic hydrocarbons (PAHs), linear alkanes, long chain alkanes, Grob's test mixture, aromatic hydrocarbons, and racemates were successfully separated on the HOCMS-coated column. The results indicate great potential for HOCMS as a novel chiral stationary phase for high-resolution GC.

## 2. Experimental

### 2.1. Chemicals and reagents

All chemicals and reagents were at least of analytical grade. Benzene, *n*-butylbenzene, toluene, *n*-propylbenzene, ethylbenzene, isomeric nitroanilines, chloroanilines, bromoanilines, iodoanilines,  $\alpha,\beta$ -ionone, and dinitrobenzene were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). The analytes used for evaluation of chromatographic performance, 2,6-dimethylaniline, 2,3-butanediol, 2,6-dimethylphenol, 1-octanol, methyl decanoate, methyl undecanoate, dicyclohexylamine, *n*-decane, *n*-undecane, *n*-dodecane, *n*-tridecane, *n*-tetradecane, *n*-pentadecane, *n*-hexadecane, *n*-tetratriacontane, *n*-pentatriacontane, *n*-hexatriacontane, *n*-heptadecane, *n*-octatriacontane, acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, chrysene and benzo[a]pyrene were purchased from Beijing Chemical Reagent Company (Beijing, China). 3-Buten-2-ol, citronellal, 2-methylvaleraldehyde, linalool, oxidized styrene, dihydrocarvyl acetate, limonene, 2-chloropropionic acid, phenylglycine methyl ester, 2-amino-1-butanol, phenylglycine, isoleucine, threonine, aspartic acid and valine were purchased from Sigma-Aldrich (St. Louis, MO, USA). Tetraethoxysilane (TEOS) (Adamas-beta, Shanghai, China), hydrochloric acid (Fengchuan Chemical Reagent Technology Co. Ltd., Tianjin, China), myristoyl chloride (Adamas-beta), L-alanine (Adamas-beta), acetone (Shandian Pharmaceutical, Yunnan, China), sodium hydroxide (Fengchuan, Chemical Reagent Technology Co. Ltd.), *N*-trimethoxysilylpropyl-*N,N,N*-trimethyl-ammonium chloride (TMAPS, Braunway Technology Co. Ltd., Beijing, China), and petroleum ether (Cologne Chemicals Limited, Chengdu, China) were used for the preparation of HOCMS. The untreated fused-silica capillary column was purchased from Yongnian Ruifeng Chromatogram Apparatus Co. Ltd. (Hebei, China).

### 2.2. Instrumentation

GC separations were conducted on a Shimadzu GC-2014C system (Kyoto, Japan) with a flame ionization detector (FID). Data collection and processing were carried out on N-2000 software. The GC carrier gas was nitrogen (99.999%). Thermogravimetric analysis (TGA) was carried out under air atmosphere on a ZRY-1P simultaneous thermal analyzer (Shanghai, China)

at a heating rate of 10 °C min<sup>-1</sup> from room temperature to 700 °C. Powder small angle x-ray diffraction (SA-XRD) patterns were recorded on a D/Max 2000 powder diffractometer (Rigaku) using Cu K $\alpha$  radiation (40 kV, 20 mA), at a rate of 1.0° min<sup>-1</sup> over the range 2 $\theta$  = 1.5°–8°. Scanning electron microscopy (SEM) images were collected on an XL30ESEM-TMP SEM (Philips, The Netherlands). Transmission electron microscopy (TEM) micrographs were obtained using a JEM-2100 TEM (Tokyo, Japan) at 300 kV. The circular dichroism (CD) spectrum of the HOCMS was measured on a Chirascan circular dichroism spectrometer (Applied Photophysics Ltd., Leatherhead, UK). The Brunauer–Emmett–Teller (BET) surface area was measured on a Micromeritics ASAP 2020 M+C system (Micromeritics, USA). Pore volumes were estimated based on the Barrett–Joyner–Halenda (BJH) method.

### 2.3. Synthesis of chiral stationary phase

#### 2.3.1. Synthesis of chiral surfactant (*N*-myristoyl-L-alanine sodium salt, C<sub>14</sub>-L-AlaA)

L-alanine (8.9 g, 0.1 mol) and NaOH (4.0 g) were dissolved in a mixture of deionized water (120 mL) and acetone (80 mL) with stirring at 5 °C. The pH of the solution was adjusted to 12.0–12.5 with NaOH solution (4.0 M). Myristoyl chloride (26.8 g, 0.11 mol) and NaOH solution (4.0 M) were then added dropwise to the reaction mixture, maintaining a pH of 12.0–12.5. After 1 h of dropwise addition, the reaction system was maintained at a pH of 12 for ~2 h. Finally, the pH of the reaction system was adjusted to 1 with concentrated hydrochloric acid to obtain C<sub>14</sub>-L-AlaA. The solid was washed with deionized water until neutral, washed five times with petroleum ether and dried at 50 °C in vacuum.

#### 2.3.2. Synthesis of highly ordered chiral mesoporous silica

HOCMS was synthesized in accordance with the method of Che et al [18]. It was prepared based on the self-assembly of chiral anionic surfactants and inorganic precursors by using TMAPS as a CSDA [30]. The negatively charged head groups provided by the anionic surfactants interact electrostatically with the positively charged ammonium sites provided by the CSDA (Fig. S1). The silica framework can then be formed by self-assembly when the alkoxy-silane groups of the CSDA co-condense with tetraalkoxysilane. In a typical synthesis, C<sub>14</sub>-L-AlaA (0.29 g, 1 mmol) was dissolved in deionized water (20.5 mL) with stirring at room temperature for 20 min. 0.1 M NaOH (8.5 g, 0.16 mmol) was added to the surfactant solution under vigorous stirring at room temperature. After the mixture had been stirred for 1 h, a mixture of 1.50 g TEOS and 0.26 g TMAPS (50% in methanol) was added to the mixture with stirring at 22 °C for 20 min. The reaction was then allowed to stand at 22 °C for 2 h. The chiral mesostructured product thus formed was cured at 60 °C for an additional 15 h. The product was recovered by centrifugal separation, washing, and drying at 60 °C. Both the anionic surfactant and the organics of the CSDA used were removed by calcination at 550 °C for 6 h. HOCMS retains local chirality and mesoporous structure during removal of the template by high-temperature calcination, and the chiral mesostructure of the surfactant is replicated in HOCMS.

### 2.4. Preparation of the HOCMS-coated capillary column

The tubular column (15 m long  $\times$  0.25 mm i.d.) coated with HOCMS was prepared by a dynamic coating method using a mixture of polysiloxane OV-1701 and an ethanol suspension of the chiral mesoporous material. An untreated fused-silica open tubular column (15 m long  $\times$  0.25 mm i.d.) was pretreated according to the following method before dynamic coating: the column was washed with 1.0 M NaOH for 3 h, ultrapure water for 1 h and 0.1 M HCl for 2 h, and then again with ultrapure water until the outflow pH was

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