



Self-assembled cyclodextrin-modified gold nanoparticles on silica beads as stationary phase for chiral liquid chromatography and hydrophilic interaction chromatography

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ABSTRACT

A facile strategy based on self-assembly of Au nanoparticles (AuNPs) (60 ± 10 nm in size) on the surfaces of amino-functionalized porous silica spheres under mild conditions was proposed. The resulting material possessed a core-shell structure in which AuNPs were the shell and silica spheres were the core. Then, thiolated-β-cyclodextrin (SH-β-CD) was covalently attached onto the AuNPs as chiral selector for the enantioseparation. The resultant packing material was evaluated by high-performance liquid chromatography (HPLC). The separations of nine pairs of enantiomers were achieved by using the new chiral stationary phase (CSP) in the reversed-phase liquid chromatography (RPLC) mode, respectively. The results showed the new CSP have more sufficient interaction with the analytes due to the existence of AuNPs on silica surfaces, resulting in faster mass transfer rate, compared with β-CD modified silica column. The result shed light on potential usage of chemical modified NPs as chiral selector for enantioseparation based on HPLC. In addition, the new phase was also used in hydrophilic interaction liquid chromatography (HILIC) to separate polar compounds and highly hydrophilic compounds.

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1. Introduction

In the past two decades, there has been great interest in the development and application of chiral chromatography, particularly in the pharmacy [1,2]. Currently, a number of chiral stationary phases (CSPs) have been described in the literature for HPLC, which have been shown to be efficient for the separation of enantiomeric compounds [3–14]. Although many CSPs are commercially available, there is a need to develop new packing materials offering higher enantioselectivity in short analysis time.

Nanomaterials have attracted much scientific and technological attention due to their excellent physical and chemical characteristics. They have been widely used in various fields such as pharmaceutical industries [15–17], chemistry, physics, material science [18], optics [19], etc. Nowadays, nanomaterials also paid more and more attention for their potential application in chromatographic separation field. Nanoparticles (NPs) with large surface-to-volume ratio and specific physical chemical properties can be easily modified with chiral selectors and increase column capacity,

separation selectivity and efficiency for chiral chromatographic separation.

Recently, the using of Au nanoparticles (AuNPs) is more and more popular in chromatographic separation science. Thiolated β-cyclodextrin (SH-β-CD) modified AuNPs based on pseudostationary phase-CEC for enantioseparation were prepared by Li etc. [20]. The results showed that SH-β-CD modified AuNPs have more sufficient interaction with analytes, resulting in significant enhancement of enantioseparation. A novel silica monolithic stationary phase functionalized with octadecanethiol gold nanoparticles (GNPs) as capillary electrochromatography was made by Ye et al. [21]. Four selected polar phenols were tested on the prepared Silica, thiol-modified silica monolith (Silica-SH), and Silica-GNPs-C18. The results revealed that Silica-GNPs-C18 column exhibits good separation. Kobayashi et al. [22] used three types of thiol compounds (noctadecanethiol, thiophenol, and 2-phenylethanethiol) to modify Au-coated polystyrene particles and prepared new stationary phases for capillary HPLC. Specific retention in thiol-modified Au columns can be used to achieve unique separation behavior. Liu and Huang [23] successfully synthesized Open Tubular Capillary Electrophoresis Chromatography columns which were modified with AuNPs by layer-by-layer assembly. Therefore, it can be found that AuNPs have shown great potential for separation science.

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The traditional CSPs are usually based on different chiral selectors on substrate surface. In this work, AuNPs were introduced into the traditional CSP to obtain a large surface to interact with analytes, thus in order to the observed improvement of enantioseparation. A new SiO₂@AuNPs-SH-β-CD core/shell CSP was prepared. The purpose of the present study is to illustrate the preparation strategy and further characterize the chromatographic properties of the CSP in detail. The effects of key parameters on the enantioseparation were investigated to illuminate characteristics of the new CSP and special selective of AuNPs.

2. Experimental

2.1. Material and reagents

Spherical silica (5 μm particle size; 10 nm pore size; 400 m² g⁻¹ surface area) was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (Lanzhou, China). 3-Amino propyl trimethoxysilane (APTMS) was obtained from Alfa Aesar (Karlsruhe, Germany). Trisodium citrate, flavanone, propranolol, R,S-equal, 6-hydroxyflavanone and gold (III) chloride hydrate (HAuCl₄·4H₂O, ≥ 99%) were purchased from CIVI-CHEMICAL Technology Co., Ltd. (Shanghai, China). Thymine, adenine, adenosine, cytosine, inosine, and guanosine were from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Hydroxylamine hydrochloride, potassium carbonate (K₂CO₃), β-CD, p-toluenesulfonyl chloride, trichloroethylene (TCE) and sodium borohydride were from Kermiyou Chemical Reagent Co., Ltd. (Tianjin, China). Fenthion, chlorpyrifos, chlorpyrifos-methyl, diazinon and fenchlorphos were purchased from Aladdin reagent database Inc. (Shanghai, China). Acetonitrile (ACN) and methanol (MeOH) of HPLC grade was from Dima Technology (Richmond Hill, ONT, Canada). All other reagents were of analytical-reagent grade (Tianjin Chemicals, China). Deionized water (> 18 MΩ cm⁻¹) was used throughout the experiments. The molecular structures of these enantiomers are presented in Fig. 1.

2.2. Instrumentation and chromatographic conditions

Transmission Electron Microscopy (TEM) images were obtained on an H-7500 TEM spectrometer (Hitachi, Japan). UV-visible spectra were acquired with a Shimadzu UV-2400 spectrophotometer. X-ray diffraction (XRD) pattern was recorded on a D8 Advance X-ray diffractometer that uses graphite-monochromated Cu K radiation. IR spectra were obtained on a Nicolet 20 NEXUS 670 FT-IR (Madison, USA) using KBr pellets. Elemental analysis was measured on a Vario EL elemental analysis system (Elementar, Germany). Field emission scanning electron microscopy (FE-SEM) images were obtained on a Hitachi S-4800.

The new separation material was slurry-packed into a 150 mm × 4.6 mm I. D. stainless steel column and acetone was used as the packing solvent at 60 MPa pressure. Evaluation of the SiO₂@Au-SH-β-CD CSP column was performed using FL2200 system (Wenling, China). The YMC chiral β-CD column (150 mm × 4.6 mm I. D., 5 μm) was obtained from YMC corporation (Japan). All the test probes were prepared to about 200 μg/mL concentration using methanol/water (v/v, 90/10). The injected volume was 5 μL. Elution was performed in isocratic mode and testing to maximal pressure resistance was 13 MPa at a mobile-phase flow rate of 1.0 mL/min for the new column. If not otherwise stated, column temperature was 25 °C. The void volume was 1.90 mL, which was determined by injecting 1,3,5-tri-tert-butylbenzene. The column efficiency for the studied five nucleosides including thymine, adenine, adenosine, inosine and guanosine were between 600–2000 m⁻¹. Useful temperature range was from 10 °C to 60 °C. Useful pH range was from 2.0 to 8.0.

2.3. Synthesis of SiO₂@Au-SH-β-CD

2.3.1. Synthesis of AuNPs

AuNPs were synthesized by the following method: 3 mL of HAuCl₄ (0.024 M) and 500 mL of trisodium citrate (2.5 × 10⁻⁴ M) were added, and then a freshly sodium borohydride prepared (15 mL, 0.1 M) was added quickly to the mixture [24]. The solution changed from colorless to a red color. The solution was centrifuged

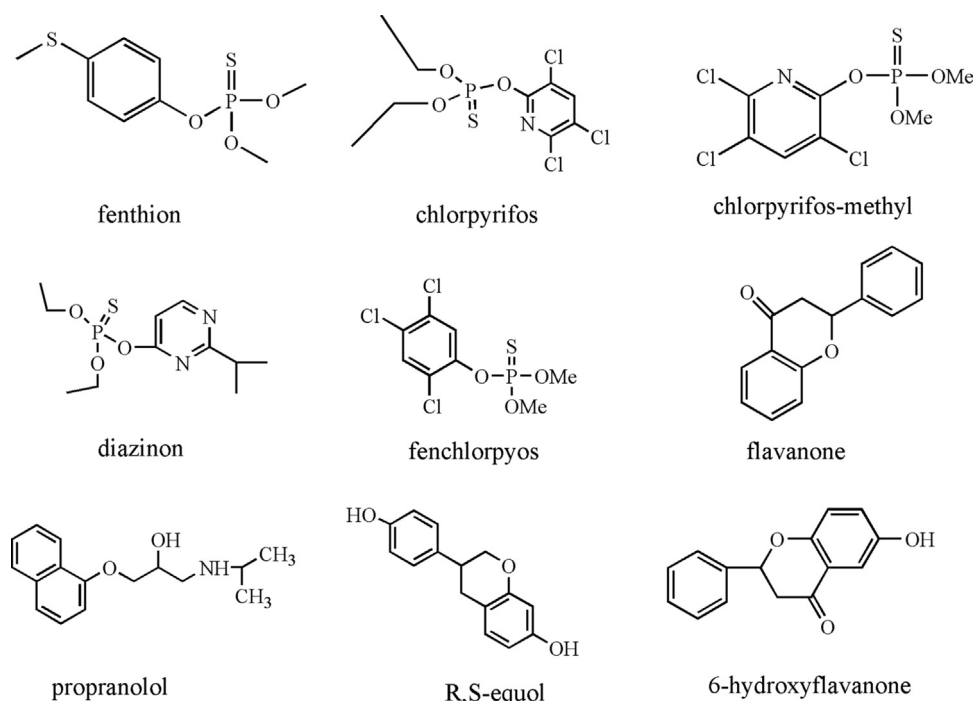


Fig. 1. Molecular structures of the test enantiomers.

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