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Chiral mesoporous organosilica spheres: Synthesis and chiral separation capacity

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ABSTRACT

New mesoporous organic–inorganic spheres with *trans*-(1*R*,2*R*)-bis-(ureido)-cyclohexane covalently bridged in the pore wall were prepared by co-condensation of *N,N*-bis-[(triethoxysilyl)propyl]-*trans*-(1*R*,2*R*)-bis-(ureido)-cyclohexane and 1,2-bis(trimethoxysilyl)ethane through a hierarchical double templating method. The octadecyltrimethylammonium chloride (C₁₈TMACl) and ethanol direct the formation of mono-dispersed hybrid spheres. *N,N*-dimethyldecylamine, acting as a pore expanding agent, can expand the pore diameter of the hybrid material from less than 1.7–10 nm during the post-synthetic treatment process. The hybrid material was employed as a novel kind of chiral stationary phase for high performance liquid chromatography (HPLC). The column packed with the hybrid material with particle size of 6–9 μm can efficiently separate the R/S-1,1'-bi-2-naphthol enantiomers even at high sample loading and high flow rate because of its high chiral ligand loading (0.93 mmol/g) and high surface area (597 m²/g).

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1. Introduction

Recently, the hybrid organosilica spheres have attracted much research interests as packing materials for high performance liquid chromatography (HPLC) because of their high mechanical and chemical stability under extreme conditions (pH < 2 and pH > 8) [1,2]. Generally, it is difficult to obtain the organosilica spheres with high surface area and uniform pore size distribution through the traditional Stöber method [3]. The “soft-templating” method associated with the sol–gel chemistry has been successfully used for the synthesis of mesoporous materials with high surface area, and ordered and tunable pore diameter [4–6].

The periodic mesoporous organosilicas (PMOs) synthesized from (RO)₃SiR'Si(OR)₃ have high surface area, tunable surface properties, high mechanical and chemical stabilities towards extreme pH values (below 2 and above 8) [1,7–9]. With the above mentioned merits, the PMOs with spherical morphology will be a novel kind of stationary phases for HPLC. Mesoporous phenylene-bridged organosilica spheres were reported by Fröba and co-workers, can be used as both a normal and a reversed phase through the combination of silanol groups and organic bridges in the framework [10]. Our group has prepared phenyl-functionalized mesoporous ethylene-bridged silica spheres through the “soft-templating” co-condensation method [7]. The mesoporous hybrid spheres exhibited comparable resolution efficiency and higher chemical stability un-

der basic medium than commercial phenyl-bonded silica packing materials. We have also prepared bifunctionalized mesoporous organosilica spheres with *trans*-(1*R*,2*R*)-diaminocyclohexane in the pores [11]. The material can be directly used as ligand-exchanged chiral stationary phase for resolution of racemic amino acids.

Recently, the chiral PMOs with chiral moiety (bulk vanadyl Schiff base complexes, binaphthyl group, and 1,2-diaminocyclohexane) bridged in the framework have been reported by several research groups [12–16]. Because of the large chiral moiety, a co-precursor such as TEOS or TMOS was used for the co-condensation to construct ordered mesoporous structure. These chiral mesoporous organosilicas exhibit chiral induction ability in the asymmetric catalysis. Mesoporous organosilicas with 100% of chiral moiety in the framework were reported by Polarz [17] and Ide et al. [18] through a chiral borated ethylene-bridged disilane precursor. Inagaki and co-workers reported the synthesis of chiral PMOs from a newly designed chiral (R)-(+)-1,2-bis(trimethoxysilyl)phenylethane precursor via a surfactant-mediated self-assembly approach under either basic or acidic medium [19]. However, only limited works have reported the morphology control of the chiral mesoporous organosilicas [20] and as far as we know, the application of chiral-moiety-bridged mesoporous organosilica spheres as CSPs for HPLC has not been reported.

In this paper, we describe the preparation of *trans*-(1*R*,2*R*)-bis-(ureido)-cyclohexyl-bridged organosilica spheres using a hierarchical double “soft-templating” method by co-condensation of 1,2-bis(trimethoxysilyl)ethane (BTME) and *N,N*-bis-[(triethoxysilyl)propyl]-*trans*-(1*R*,2*R*)-bis-(ureido)-cyclohexane (DACH-BS).

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The key point of this synthetic method is to control the morphology and mesostructure of the resultant material separately. The 6–9 μm mono-dispersed mesoporous organic–inorganic spheres were formed with the aid of octadecyltrimethylammonium chloride ($\text{C}_{18}\text{TMACl}$) and ethanol. The pore diameter of the hybrid material was enlarged from less than 1.7–10 nm with slight increase of pore volume and surface area using *N,N*-dimethyldecylamine as pore expansion agent. The DACH-BS-bridged mesoporous organosilica spheres with high surface area (597 m^2/g), large pore diameter (10 nm), and high loading of chiral ligand (0.93 mmol/g) can act as efficient packing material for the separation of *R/S*-1,1'-bi-2-naphthol racemates. For comparison, DACH-BS was also immobilized on commercial Kromasil silica (surface area: 300 m^2/g ; pore diameter: 10 nm; particle size: 5 μm) by chemical grafting method. Under similar conditions, the column packed with DACH-BS-bridged mesoporous organosilica spheres exhibit higher separation efficiency than that with commercial Kromasil silica grafted with DACH-BS.

2. Experimental section

2.1. Chemicals

1,2-Bis(trimethoxysilyl)ethane (BTME) and *N,N*-dimethyldecylamine (DMDA) was purchased from Sigma–Aldrich. Octadecyltrimethylammonium chloride ($\text{C}_{18}\text{TMACl}$) from Nanjing Robiot (Nanjing, China) and other reagents were obtained from Shanghai Chemical Reagent of Chinese Medicine Group (Shanghai, China). *trans*-(1*R*,2*R*)-Diaminocyclohexane was separated by chiral resolution of a commercially available mixture of *cis*- and *trans*-1,2-diaminocyclohexane (30/70) according to the literature method [21]. All solvents were analytical quality and dried by standard methods. *N,N'*-bis-[(triethoxysilyl)propyl]-*trans*-(1*R*,2*R*)-bis-(ureido)-cyclohexane (DACH-BS) was synthesized according to the published method by slow addition of 3-isocyanatepropyltriethoxysilane to a solution of (1*R*,2*R*)-diaminocyclohexane under inert atmosphere [20].

2.2. Synthesis

In a typical synthesis, the surfactant $\text{C}_{18}\text{TMACl}$ (1.04 g) was dissolved in a mixture of deionized water (20.0 mL), ethanol (7.0 mL) and 1 M NaOH (11.8 mL) with stirring at 40 $^{\circ}\text{C}$ to obtain a clear solution. The solution was then cooled down to room temperature,

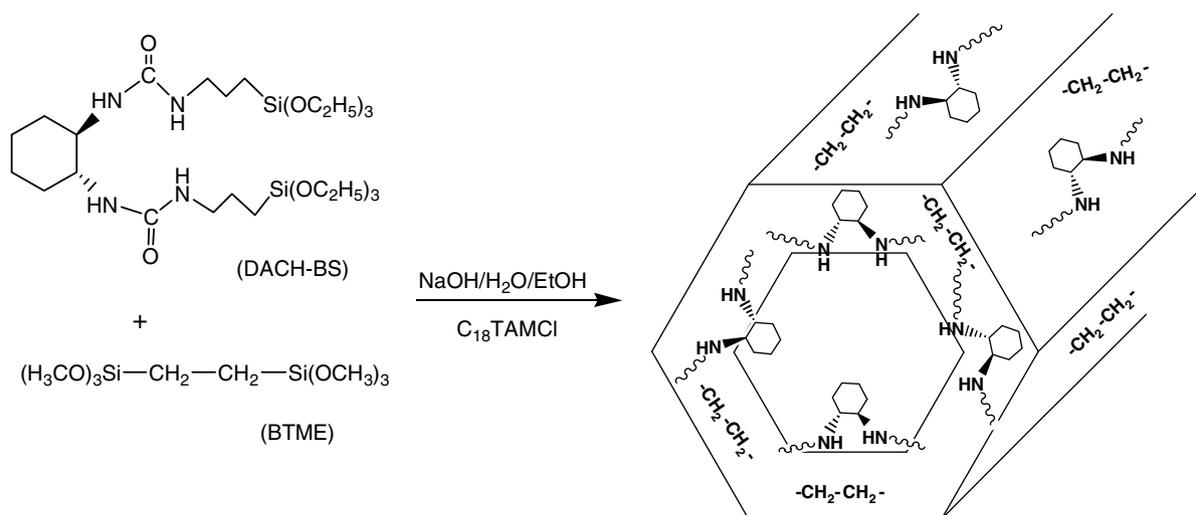
and the mixture of DACH-BS (1.01 g) and BTME (1.03 g) in 3 mL of ethanol was added to the above solution under vigorous stirring. After stirring for 30 min at room temperature, the clear solution was transferred into a Teflon-lined autoclave and kept at 80 $^{\circ}\text{C}$ for 16 h without agitation. The white precipitate was collected by filtration, washed thoroughly with distilled water, and dried at 60 $^{\circ}\text{C}$. The molar ratio is BTME 0.50–0.90/DACH-BS 0.10–0.50/ $\text{C}_{18}\text{TMACl}$ 0.60/NaOH 2.36/EtOH 34.37/ H_2O 353.60. The surfactant was removed by stirring 1.0 g of product in 200 mL of ethanol containing 2.1 g of 36% aqueous HCl solution for 6 h at 50 $^{\circ}\text{C}$. After filtration, the product was washed thoroughly with ethanol and dried in air at room temperature. This surfactant extraction treatment was performed for one more time. The materials were denoted as $\text{DACH}_B\text{-}x$, where x ($x = 10, 30, 50$) referred to the molar percent of DACH-BS/(BTME + DACH-BS). The schematic illustration for the synthesis of organosilica was shown in Scheme 1.

The as-synthesized $\text{DACH}_B\text{-}30$ (2.0 g) was added to a mixture of *N,N*-dimethyldecylamine (DMDA) (2.5 g) in distilled water (80.0 g) under magnetic stirring. The mixture was stirred for 30 min at room temperature. Then, the vessel was sealed and placed in an oven at 120 $^{\circ}\text{C}$ under static condition for three days. The product was recovered by filtration, washed with deionized water, and dried under ambient conditions. The surfactant extraction process was similar to $\text{DACH}_B\text{-}30$. This material was denoted as $\text{EDACH}_B\text{-}30$.

End-capping of silanols was obtained by refluxing of $\text{EDACH}_B\text{-}30$ (1.0 g, dried under vacuum at 120 $^{\circ}\text{C}$ for 24 h) and trimethylethoxysilane (3 mL) in dry toluene (20 mL) for 8 h under argon atmosphere. After filtration, the product was washed with toluene and methanol, and dried in air. This material was denoted as $\text{EEDACH}_B\text{-}30$.

2.3. Grafting of DACH onto commercial SiO_2 (DACH- SiO_2)

After drying in vacuum oven at 120 $^{\circ}\text{C}$ for 24 h, Kromasil silica (1.0 g) (surface area: 300 m^2/g ; pore diameter: 10 nm; particle size: 5 μm ; EKA Nobel, Sweden) was placed in a three-necked round bottom flask equipped with a reflux condenser and inert gas inlet. Dry toluene (20 mL) was added followed by the addition of DACH-BS (0.61 g). The mixture was heated to reflux with stirring for 8 h under argon atmosphere. After cooling down to room temperature, the powder product was filtered and washed thoroughly with toluene and methanol, and dried under vacuum at 60 $^{\circ}\text{C}$ overnight. This material was denoted as DACH- SiO_2 .



Scheme 1. The scheme of the synthesis process for the *trans*-(1*R*,2*R*)-bis-(ureido)-cyclohexane bridged organosilicas.

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