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Fabrication of silica monolithic columns with ordered meso/macropore structure

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ABSTRACT

Recently, much effort has been focused on the materials with ordered meso/macropores, because of their potential applications in catalysis, separations, coatings, microelectronics and electro-optics. In this paper, silica monoliths with well-defined columnar shape more than 1 cm in length are successfully fabricated by using the micelles of triblock copolymer F127 and colloidal crystals composed of polystyrene (PS) latex microspheres as mesopore and macropore template, respectively. The column templated by PS microspheres 870 nm in diameter and 0.5 g F127 (MCL-0.5-870) shows uniform ordered macropores, contact pores connecting macropores together, and assembled and inter-particle pores increasing the BET specific surface area and adsorption capability of the monolithic column. The backpressure curve and hydraulic permeability experiment exhibit its good penetrability and mechanical stability. These excellent characteristics, together with high BET specific surface area (387.4 $m^2 g^{-1}$) and porosity (80%), may endow its potential application for chromatography separation. In addition, the size of macropores and mesopores can be easily regulated by changing the diameter of PS spheres and F127 weight, respectively. This indicates that this method is a facile and universal protocol to fabricate the applied monolithic column with ordered meso/macropores.

1. Introduction

In recent years, the monolithic column with meso/macropores is increasingly recognized as a good alternative to the particle-packed column for high efficiency separations in the high-performance liquid chromatography (HPLC), capillary electrochromatography (CEC), nano-liquid chromatography (nano-LC), etc. [1–3]. Generally, based on the component of materials, the monolithic column can be classified into two categories: organic [1,4] and inorganic monolithic columns [5–7]. Since the silica has many merits, such as facile fabrication, high mechanical strength and thermal stability, it becomes the most widely and systematically investigated medium in the inorganic monolithic columns [8]. Nowadays, the silica monolithic column is often prepared by a sol–gel process, whose macropore formation is a competitive process involving the phase separation and sol–gel transition. The size and distribution of macropores in this kind of column can be regulated by changing the fabrication conditions, such as the molar ratio between silicon source and phase-separation reagent [5]. However, these macropores are usually unordered and weakly interconnected, which may decrease the rate of mass transfer in them. According to the principles reported by Gzil and his coworkers [9,10], monolithic columns with uniformly periodic pores and high porosity may display high separation efficiency. Thus, it may be a trend to fabricate monolithic columns with ordered hierarchical pores in the development of new chromatographic media.

Until now, the materials with ordered meso/macropores are often prepared by a dual templating method [11–15]. The supramolecular system based on self-assembly, such as micelles composed of triblock copolymer (for example, F127 or P123) or surfactant (for example, CTAB), is usually utilized as one template to direct the formation of mesopores; while colloidal crystals are used as another template to produce macropores. The dimension of macropores and mesopores can be easily controlled by varying the microparticle size of colloidal crystals and concentration or composition of triblock copolymer, respectively. However, most of acquired materials are flake-like monoliths to date [14,15], which are not suitable to use as chromatographic media.

In this paper, the silica monolithic column more than 1 cm in length with ordered meso/macropores were fabricated by using the polystyrene (PS) colloidal crystal and triblock copolymer F127 as dual templates. In order to get long monolithic columns, the isothermal heating evaporation-induced self-assembly (IHEISA) method [16] was firstly extended to synthesize the colloidal-crystal template. The as-prepared silica monolithic columns were extensively characterized by the scanning electron microscope (SEM), transmission electron microscope (TEM), nitrogen adsorption–desorption isotherm, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Furthermore, their hydrodynamic properties including the backpressure curve and hydraulic permeability were determined.

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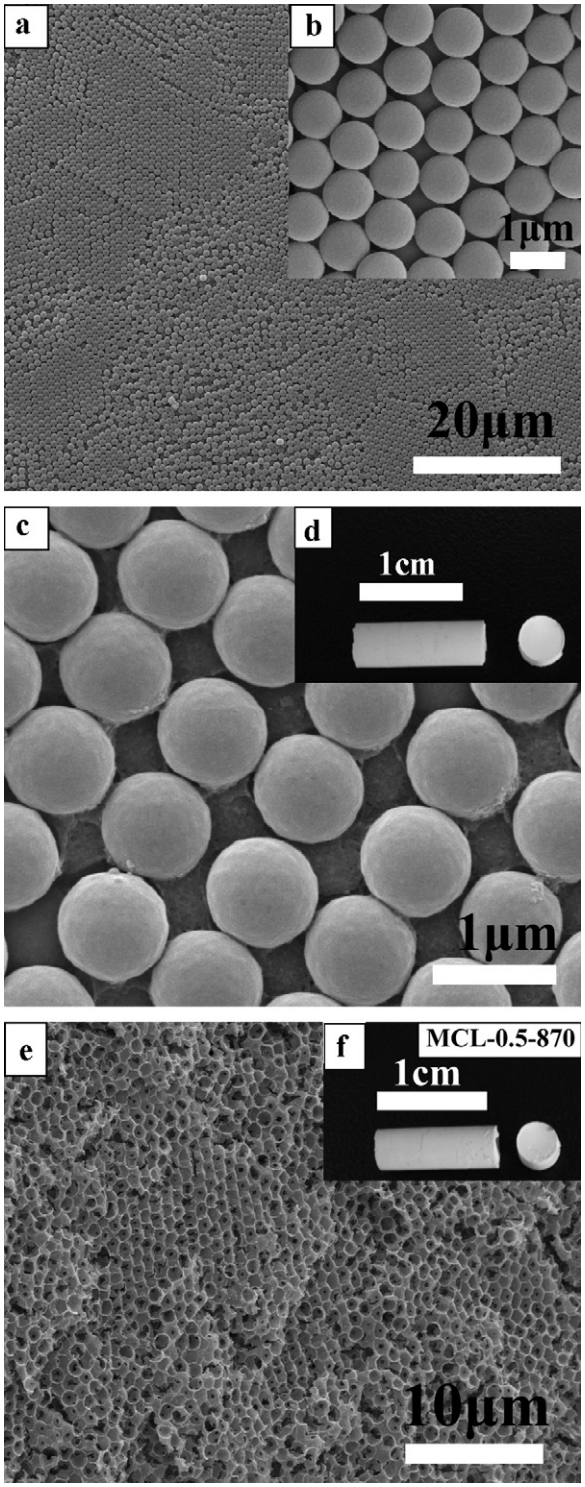

Fig. 1. SEM images of colloidal crystals composed of PS spheres about 870 nm in size (a and b) and MCL-0.5-870 before (c) and after (e) calcination. The insets (d) and (f) show the corresponding digital pictures of (c) and (e), respectively.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%) and triblock copolymer F127 ($EO_{106}PO_{70}EO_{106}$, average molecular weight 12, 600) were purchased from Sigma–Aldrich, and used as received. Styrene (St, 98%) was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Before use, styrene was extracted with 10% aqueous solution of NaOH and distilled water, respectively, dried over anhydrous $MgSO_4$, and then distilled under vacuum. Other reagents were analytical grade and used as received. De-ionized water was used throughout the study.

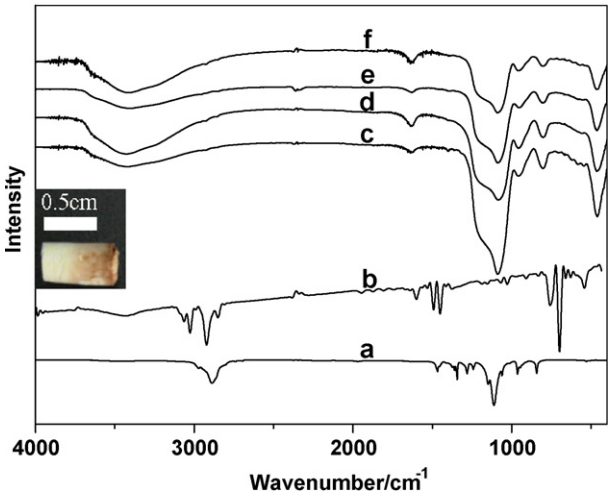

Fig. 2. FTIR spectra of F127 (a), PS spheres (b), and composites of PS colloidal crystals with silica gel after calcined at 500 °C for 8 h (c), 6 h (d), 4 h (e) and 2 h (f). The inset shows the digital picture of the composites after calcined for 2 h.

2.2. Preparation of PS colloidal crystals

Monodisperse PS latex particles were prepared by a soap-free emulsion polymerization reported in the literature [17]. The average diameters of acquired PS spheres were calculated to be 820, 870, 920, and 1330 nm, respectively, by the analysis of SEM micrographs (Fig. 1a and b) [18]. Their coefficient of variation (CV) values were ca. 1.21%, 2.27%, 1.45% and 4.72%, respectively. PS colloidal crystals in a void chromatographic column of 50 mm × 4.6 mm I.D. were prepared by a modified isothermal heating evaporation-induced self-assembly (IHEISA) method [16]. Simply, PS spheres were dispersed in ethanol and diluted to be 1 wt.% at first. Then, the colloidal solution was added into the column drop by drop, which was kept in a thermostat at 45 °C without disturbance for 12 h. This process was repeated several times until the length of PS colloidal crystals reached about 1.5 cm.

2.3. Fabrication of silica monolithic columns

In a typical synthesis, 7 mL of 0.136 M HCl was added into 12 mL TEOS under stirring at room temperature for 0.5 h, and then a certain weight of F127 was dissolved in the above solution under vigorously stirring for another 1 h. The mixture was added into the chromatographic column containing PS colloidal crystals, which was connected to the pre-column containing silica precursor via PEEK tube. Subsequently, the whole apparatus were connected to an HPLC, and washed with ethanol for 12 h at the flow rate of 0.004 mL min^{-1}. After dismounted from HPLC and sealed, the column was heated in water bath at 50 °C for 12 h, and then kept at room

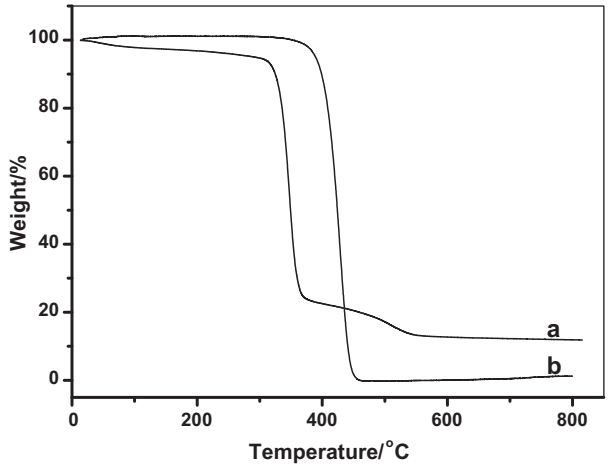

Fig. 3. TGA curves of the composites of PS colloidal crystals with silica gel (a) and dried PS colloidal crystals (b) in air atmosphere.