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A facile route to a silica monolith with ordered mesopores and tunable through pores by using hydrophilic urea formaldehyde resin as a template

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Abstract

In this paper, bi-continuous silica monolith with highly ordered mesopores and tunable through pores (macropores or macro channels) has been successfully synthesized through nanocasting method. The starting urea formaldehyde (UF) resin, which is hydrophilic and contains adjustable through pores in micrometer scale, was for the first time used as a hard template in nanocasting. The silica replica has the same macroscopic morphology and macropore structure as the starting UF resin template, indicating that the macropores in silica monolith could also be adjusted. More interestingly, long-range ordered domains with highly ordered mesopores of hexagonal arrays existed in the frameworks of the silica monolith.

Keywords: Bi-continuous; Silica monolith; UF resin; Ordered mesopores; Nanocasting; Hexagonal

1. Introduction

Ordered mesoporous materials have attracted great attention since their discovery in 1992 [1,2]. Generally, these materials have been synthesized by using inorganic precursors in the presence of surfactant. Due to the fascinating structures of high specific surface areas and large uniform pore sizes, this class of materials has many potential applications in catalysis, separations, optical materials, sensors, and so on.

To date, ordered mesoporous materials are available in the forms of fine powders [3–5], fibers [6,7], thin films [8] and even monoliths [9–16]. For advanced application, it is important that fabricates ordered mesoporous materials into monolithic shape. Several groups reported crack free silica monolith with ordered mesostructure [9–11], but the lack of macro channels (through pores or macropores) limited the practical application of the obtained monolithic materials. Later, Huesing [12,13], Feng [14] and Nakanishi [15,16] developed monolithic silica materials with periodically arranged mesopores and continuous macro channels by sol–gel process. When the ordered mesoporous material is combined with monolithic morphology and continuous macro channels, a lot of benefits will arise. Firstly, the macroscopic shape will improve processability of the materials; secondly, the co-existence of through pores provide fast diffusion channels for molecules especially large molecules such as DNA, polymer to transport to the mesoporous surface of the monolith, leading to higher separation or catalytic efficiency, etc.

Although sol–gel method for the synthesis of ordered monolith with through pores is very simple, it is not suitable for the case that materials could not form sol under usual conditions, which limited the universality of this sol–gel method. Nanocasting is another choice, which is parallel to the sol–gel method in preparing novel mesostructured materials [17–19]. This strategy was originally evolved from the porous Al_2O_3 membrane templating

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method [20] and first applied to the preparation mesoporous carbon [21]. With performed mesoporous materials serving as a confined reactor or growing space, inorganic precursors are incorporated into the mesopores, and after removal of the templates, the nanomaterials can completely maintain the topologies of the templates to achieve interesting replica mesostructures.

Here, we adopted nanocasting method and proposed a new template urea formaldehyde (UF) resin for the preparation of silica monolith with highly ordered mesopores and tunable macro channels. Compared to the templates reported previously, such as silica [22–25], polystyrene [26], polyurethane foam [27], carbon [28,29] and starch gel [30,31], the UF resin template has the advantages of being readily available, inexpensive, and easy to process. In addition, precursors without organic solvents could be applied in the synthetic procedure because of the hydrophilic nature of the template. Therefore, it should be low-cost, environmentally benign, and amenable to be scaled-up.

2. Experimental

2.1. Materials and reagents

Tetraethyl orthosilicate (TEOS, 95%) was obtained from the Chemical Factory of Wuhan University (Wuhan, China). Poly(alkylene oxide) block copolymer (abbreviated as $EO_{20}PO_{70}EO_{20}$, P123) was a gift from BASF (USA). Poly(ethylene glycol) (PEG, $M_w = 6000$), formaldehyde (36%), urea, glycerol, hydrochloric acid (38%), sodium hydroxide and ethanol were of analytical grade and were purchased from Shanghai General Chemical Reagent Factory (Shanghai, China). Distilled water was from a quartz apparatus.

2.2. Preparation of the urea formaldehyde (UF) resin template

Formaldehyde solution (83.3 g) with 7 g glycerol and 36 g urea was mixed and the pH of the mixture was adjusted to 7–8 by sodium hydroxide solution, a milk like prepolymer of the UF resin was obtained after the solution was refluxed for 4 h. And then 9 ml of HCl ($pH \approx 2$) and 1.2 g of PEG were added to the prepolymer. After being stirred for half an hour, the mixture was transferred to a deposable polypropylene syringe to solidify at 298 K for 24 h. Finally, a monolithic UF resin (designated as UF-1) which fully copied the shape of the reaction vessel was acquired.

2.3. Preparation of the colloidal silica

The silica sol was prepared according to a previous reported method [32]. Briefly, 1.10 ml of TEOS was mixed with 0.54 ml of HCl (0.01 mol/L) and 1.52 ml of ethanol under vigorous stirring at room temperature. After stirring for 20 min at 293 K, 0.275 g of P123, which was dissolved in 1.00 ml of ethanol, was added to the prehydrolyzed silica solution. The TEOS/P123/ethanol/HCl (H_2O) molar composition in the final sol was 1.00:0.01:8.69:6.00.

2.4. Preparation of the silica replica from the UF resin template

The UF-1 was firstly immersed in the colloidal silica for 15 min. Then it was removed from the solution, and was allowed to dry at 303 K for 2 h. The same procedure was repeated for six times. The as-synthesized composite monolith was calcined at 773 K for 6 h (ramped at 1 K/min) to burn off the UF resin template and block copolymer of P123. Finally, white, crack free monolithic silica was acquired (designated as silica-1). The silica material investigated throughout the paper referred to silica-1 unless specified.

2.5. Characterization of the silica monolith

Elemental analysis was performed with a Flash-1112 Series elemental analyzer (Milan, Italy). Scan electron microscope (SEM) experiments were performed with Hitachi Model X-650 scanning electron microscope instrument (Tokyo, Japan). Slices of cross sections were cut off from the UF resin template and the silica monolith, and were vapor-deposited with gold for scanning electron microscope analysis at 25 kV. The TEM image of the silica monolith was recorded on JEOL JEM-2010 HT transmission electron microscope (TEM) with an operating voltage of 200 kV. X-ray powder diffraction (XRD) experiment was carried out on a D8-Advance X-ray diffractometer (Bruker, Germany) using Cu Kα radiation ($\lambda = 0.154060$ nm) to investigate the internal array of the silica monolith. The porous structure of the silica monolith was measured with an Autopore IV 9510 mercury porosimeter (Micromeritics, USA) and Coutler SA 3100 Plus analyzer (Florida, USA). The specific surface area value was calculated according to the BET (Brunauer–Emmett–Teller) equation at P/P_0 between 0.05 and 0.2. The pore size distribution was calculated from the desorption isotherm using the BJH (Barrett–Joyner–Halenda) method. The monolithic sample was activated by evacuating in vacuum and heating to 433 K for 10 h to remove any physically adsorbed materials before analysis.

3. Results and discussion

3.1. The composition and morphology of the silica monolith

A silica monolith was chosen as a representative for elemental analysis (EA) to determine the carbon residue. The EA result demonstrated that less than 0.4 wt% carbon could be detected in the final silica monolith, suggesting a nearly complete removal of the UF resin template.

Fig. 1 shows a photograph of the UF resin template, UF-silica composite and the resulted silica replica.