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Silicone surfactant templated mesoporous silica

Ji Feng, Bo Sun, Yuan Yao *, Shunai Che *

School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Key Laboratory for Thin Film and Microfabrication Technology of the Ministry of Education, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China

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ABSTRACT

Tailoring the wall thickness and organo-functionalization are two important issues in the design and application of mesoporous materials. Herein we report a novel strategy to deal with such two issues simultaneously by using a commercially available silicone surfactant, an ABA-type triblock copolymer poly(ethylene oxide)-*block*-polydimethylsiloxane-*block*-poly(ethylene oxide) (PEO_{14}-*b*-$PDMS_{13}$-*b*-PEO_{14}). The silicone surfactant serves as the template for directing meso-structures, the source of functional groups for surface modification, and the silica source for strengthening the wall of mesochannels. Meanwhile, 1,3,5-trimethyl benzene (TMB) was employed as the pore-swelling-agent. The mesoporous silica materials with thick walls and/or hydrophobic dimethylsiloxane functionalized pores were achieved by calcination and extraction, respectively.

1. Introduction

Mesoporous silica materials are of special interest due to their unique features [1–4] and potential applications in the fields of catalysis, sensing, optically active materials, and biomaterials [5–8]. Commonly, mesoporous silica materials could be fabricated by using cationic [9–11], non-ionic [12–14] and anionic surfactants [15–18] as templates to obtain ordered mesostructures and well-controlled morphologies, pore sizes, and porosities.

Tailoring the wall thickness is an important issue in the design and application of mesoporous materials. Except for changing the hydrothermal treatment and aging conditions [19–21], the wall thickness could also be adjusted by tuning the length of the hydrophilic segment of template. It was found that the wall thickness of hexagonally meso-structured silica increased with the elongation of poly(ethylene oxide) $(EO)_x$ block in the Pluronic surfactant [22]. Ryoo and co-workers reported a synthetic approach for systematically controlling the wall thickness of mesoporous silica by using a mixture of PEO-containing non-ionic surfactant and cationic surfactant [23]. Recently, alkyl alcohol ether carboxylate (AEC: $C_nH_{2n+1}O(CH_2CH_2O)_mCH_2COONa$) surfactant was applied to fabricate hexagonal mesoporous silica with thick walls. The two types of hydrophilic head groups led to the formation of unique double-layer silica walls and the wall thickness were obviously increased as a result [24].

Organo-functionalization is also an important issue to combine enormous functions with the high surface area, uniform pore size, and thermally stable inorganic substrates [25–28]. The organo-functionalized mesoporous materials have been prepared through several distinct routes yet: (i) the post-grafting method [29–35]; (ii) the co-condensation method [36–40]; (iii) introduction of co-structure directing agent [15–18] and (iv) the application of special precursors and templates such as bissilylated single-source organosilica [41–46] and surfactants consisting of functionalized condensable heads and cleavable alkyl tails [47].

Here we report a facile strategy to thicken the walls of mesoporous silica materials and hydrophobically functionalize the surface of channels by using a commercially available silicone surfactant Q4-3667 as template. Q4-3667 is an ABA type triblock copolymer, PEO_{14}-*b*-$PDMS_{13}$-*b*-PEO_{14}. The PDMS block not only acts as the templates for pore formation, but also offers dimethyl siloxane segments for obtaining hydrophobic surface. In addition, the PDMS block also provides the silica source for thickening the walls by calcination. As shown in Scheme 1b, the PDMS block could form Si–O–Si inorganic network while be calcined at a high temperature (550 °C), which offers a new pathway to thicken the silica walls of the mesoporous materials. On the other hand, the PDMS blocks could attach to the silica matrix to achieve hydrophobic functionalization on the walls. However, the disadvantage of this strategy is that PDMS might fill up the pores (Scheme 1a) and prevent other molecules from entering into the mesochannels. In order to solve this problem, 1,3,5-trimethyl benzene (TMB) was employed as the pore-swelling agent [48,49]. The hydrophobic TMB was expected to swell up the hydrophobic part of the micelles of Q4-3667 by stabilizing the oil/water interface due to the hydrophobic interaction with the PDMS chains (Scheme 1c), and further tune the pore size of mesoporous silica. After the silica matrix was formed, TMB could be removed by extraction to obtain accessible dimethyl siloxane functionalized mesopores (Scheme 1d).

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* Corresponding authors. Tel.: +86 21 5474 2852; fax: +86 21 5474 5365.
E-mail addresses: yaoyuan@sjtu.edu.cn (Y. Yao), chesa@sjtu.edu.cn (S. Che).

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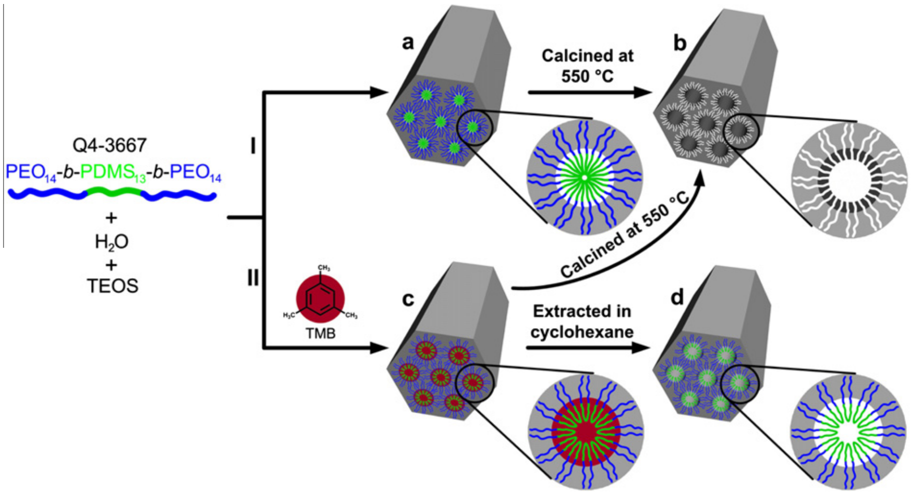

Scheme 1. Schematic illustration of the synthetic routes to the formation of Q4-3667 directed mesostructure (a), mesoporous silica with thick wall (b), organo-functionalized mesoporous silica with addition of TMB (c) and subsequent extraction (d). The black part of the cross section view in (b) denoted the deoxidized product of the PDMS chains.

2. Experimental

2.1. Materials

Q4-3667 was provided by Dow Corning Corporation. 1,3,5-trimethyl benzene (TMB) and tetraethoxysilane (TEOS) were purchased from Sinopharm Chemical Reagent Co., Ltd. All these reagents were used as received.

2.2. A representative synthetic method

1.0 g of Q4-3667, 0, 0.4 or 0.8 g of TMB and 108.6 g of deionized water were mixed to form a homogeneous solution. The solution was heated to 35 °C prior to the addition of TEOS. After the addition of TEOS (2.97 g), the mixture was stirred for 30 min, followed by reaction under the static condition for one day at 35 °C. The mixture was sealed in a Teflon autoclave and aged at 100 °C for two days. The reaction was carried out in a sealed vessel throughout the whole synthetic process. The solid product was collected by filtration or centrifugation, washed with water, and dried in air at 60 °C. The resultant powder was either calcined at a 2 °C/min heating rate from room temperature to 550 °C and held for 6 h in air to simultaneously remove the template and TMB, or extracted in cyclohexane at 80 °C for 48 h to remove TMB. The feed mass composition was Q4-3667:H_2O:TMB:TEOS = 1:108.6:x:2.97. The as-made samples were denoted as SMS-0-as (with no TMB), SMS-0.4-as (with TMB/Q4-3667 (w/w) = 0.4/1) and SMS-0.8-as (with TMB/Q4-3667 (w/w) = 0.8/1), respectively. The corresponding calcined samples and extracted samples were denoted as SMS-0-cal, SMS-0.4-cal and SMS-0.8-cal, and SMS-0.4-ex and SMS-0.8-ex.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer D/MAX-2200/PC equipped with Cu Kα radiation (40 kV, 20 mA) at the rate of 0.1 deg./min over the range of 1–6°(2θ). HRTEM was performed with a JEOL JEM-3010 microscope operating at 300 kV (Cs = 0.6 mm, resolution 1.7 nm). Images were recorded with the Kodak electron film SO-163 using low-electron-dose conditions. The nitrogen adsorption/desorption isotherms were measured at 77 K with the Quantachrome Nova 4200E. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method and the pore size was obtained from the maxima of the pore size distribution curve calculated by the Barett-Joyner-Halenda (BJH) method using both the desorption and adsorption branch of the isotherm. The pore volumes of the mesopores and micropores were estimated by BJH and t-plot method base on the desorption branch of the isotherm. Solid-state ^{13}C CP/MAS NMR spectra were collected on an Oxford AS400 NMR spectrometer at 100 MHz and a sample spinning frequency of 3 kHz.

3. Results and discussion

The XRD patterns of the as-made, extracted and calcined samples synthesized with different TMB/Q4-3667 ratios are shown in Fig. 1. All samples show three well-resolved reflection peaks with a d-spacing ratio of $1:\sqrt{3}:2$, which can be indexed as (10), (11) and (20) reflections of the two dimensional (2D)-hexagonal *p*6*mm* structure. The unit cell parameter a of the SMS-0-as was 8.9 nm. The diffraction peaks of the samples SMS-0.4-as and SMS-0.8-as shifted toward low angle and their unit cell parameters increased to 9.3 and 9.7 nm, respectively because TMB swelled the hydrophobic cores of the micelles [50–53]. As shown in Fig. 1B, the diffraction peaks of all calcined samples shifted toward high angles. The unit cell parameters of the SMS-0-cal, SMS-0.4-cal and SMS-0.8-cal decreased to 8.5, 8.6, and 8.9 nm respectively because of the shrinkage of the silica frameworks. Compared to the as-made samples, the unit cell parameters of the SMS-0.4-ex and SMS-0.8-ex that were calculated from the XRD patterns shown in Fig. 1C also decreased to 9.0 and 9.3 nm respectively due to the shrinkage of the silica matrix.

As shown in Fig. 2, the corresponding high-resolution transmission electron microscopy (HRTEM) images with the typical hexagonal *p*6*mm* array of (10) plane of the calcined samples, which were consistent with the XRD results. The center-to-center distances of pores in these three samples were 8.5, 8.7, and 8.9 nm for SMS-0-cal, SMS-0.4-cal and SMS-0.8-cal, respectively, which were close to the unit cell parameters calculated based on the XRD patterns.

The isotherms of the calcined samples displayed type IV curves with H2-type hysteresis loops, indicating the existence of ink-bottle style mesopore channel structure within the materials (Fig. 3A). It can be considered that the pores were not perfectly cylindrical because the PDMS chains were oxidized into silica after calcination, which may form ink-bottle style pore channel structure, and result in the H2-type hysteresis loops, although the XRD patterns and TEM images revealed the silica materials possessed ordered