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Short communication

MCM-41 mesoporous silica sheet with ordered perpendicular nanochannels for protein delivery and the assembly of Ag nanoparticles in catalytic applications

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ABSTRACT

In this study, well-ordered microscale MCM-41 mesoporous silica sheets of ca. 80 nm thicknesses were first prepared by using water and petroleum ether as cosolvents in the presence of CTAB as template and TEOS as silica precursor. The as-synthesized materials showed excellent bovine serum albumin proteins loading capacity (598 mg protein per gram silica materials), controllable sustained protein release profile, and effective catalytic reduction performance of 4-nitrophenol after high payload of Ag nanoparticles.

1. Introduction

MCM-41 mesoporous silica materials have attracted a great attention since its discovery in 1992 [1,2]. These mesoporous silica materials with uniform pore structure, high pore volume and good stability have been applied extensively in the fields of catalysis, drug delivery, protein immobilization, adsorption and separation [3,4]. Its rich morphology endows them another appealing character in many designed applications [5–7]. To date, extensive efforts have been devoted to synthesize MCM-41 materials with various morphologies, such as spheres, rods, fibers, tubes, and films [8]. However, few studies have been reported on mesoporous silica sheet form with ordered perpendicular nanochannels, which would be very favored in mass transfer applications due to its short oriented pore channels and thus easy access.

Previously, Mou and coworkers chose the cationic/anionic surfactant system, cetyltrimethylammonium bromide (CTAB)/sodium dodecylsulfate (SDS), as the confining bilayer lamellar structure and let the pluronic123/silicate nanocomposite intercalate between the bilayers to fabricate micrometer-sized SBA-15 sheets with vertical channels [9,10]. Park et al. synthesized SBA-15 sheets from the co-condensation of sodium metasilicate and amino-propyltriethoxysilane in the presence of pluronic123 under microwave irradiation in strongly acidic conditions [11]. Recently, Kato et al. firstly prepared one kind of carboxylate surfactant, N-palmitoyl-L-alanine, and then employed it in combination with pluronic123 to obtain SBA-15 sheet material [12]. All of these approaches, however, require a tedious procedure to fabricate SBA-15-type mesoporous silica sheet from pluronic123 block copolymer. In addition, MFI-type zeolite nanosheets were also emerged especially for the application of volatile organic compounds (VOC) adsorption [13–15]. However, these materials are generally needed complex surfactant and high temperature, and most importantly, the pores in these materials were not uniform and ordered. Therefore, the synthesis of well-defined mesoporous silica sheet via a simple and effective approach is still very challenging.

Herein, we first report a method for synthesizing micrometer-sized MCM-41 mesoporous silica sheets with ordered perpendicular nanochannels by simply using water and petroleum ether as cosolvents in the presence of CTAB as template and TEOS as silica precursor. Our strategy is to firstly form CTAB micells in water

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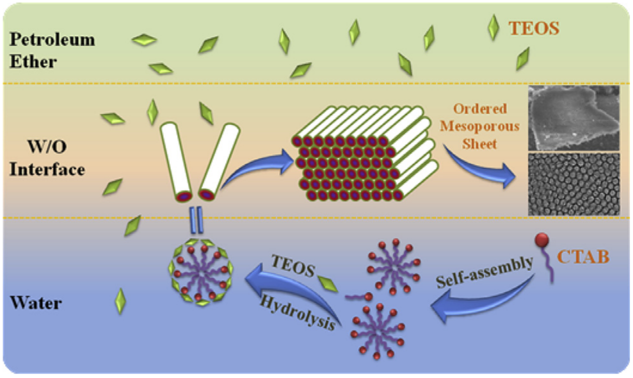

Fig. 1. Schematic illustration for the formation of MCM-41 mesoporous silica sheet.

phase, followed by the addition of TEOS in petroleum ether phase to make the formation of silica-coated micells and let its assemble in the W/O interface to obtain sheet-like structures with ordered pore channels (Fig. 1). In addition, their applications in protein delivery and catalysis were examined.

2. Experimental

2.1. Materials

Cetyltrimethylammonium bromide (CTAB), petroleum ether (boiling range from 60° to 90°), tetraethyl orthosilicate (TEOS), aqueous ammonia, $AgNO_3$, $NaBH_4$, bovine serum albumin (BSA), hydrochloric acid (HCl, 37%), and 4-nitrophenol were obtained from Beijing Chemical Reagents Company (China). All chemicals were used as received without any further purification.

2.2. Synthesis of MCM-41 mesoporous silica sheet

MCM-41 mesoporous silica sheet was synthesized by using water and petroleum ether as solvents in the presence of CTAB as template and TEOS as silica precursor. In a typical synthesis, 1.5 g CTAB was dissolved in water phase of 300 ml H_2O and 100 ml petroleum ether, and 9 ml $NH_3 \cdot H_2O$ (25%~28%) was added with gentle stirring for 30 min at room temperature. 5.4 ml TEOS was then added in ether phase with gentle stirring for another 5 h. After collected by centrifugation and followed by washed three times with ethanol. CTAB template in the nanoparticles was removed by extraction method (18 mL of 37% HCl in 300 mL of ethanol) via stirring at 70 °C for 24 h. The final nanoparticles were obtained by centrifugation at 5000 rpm for 5 min and washed with ethanol for three times. The resulting solid products were dried at 80 °C overnight for further analysis.

2.3. BSA proteins loading and release

To load BSA into the MCM-41 mesoporous silica sheet, the materials were dispersed in BSA stock solution (10 mg mL^{-1} in Phosphate Buffered Saline (PBS, pH 7.4), keeping the weight ratio of silica sheet to BSA at 1:1) and stirred for 24 h at 4 °C, followed by centrifugation and washing twice with pH 7.4 PBS to obtain the protein-loaded MCM-41 mesoporous silica sheet. The loading amount of BSA was determined by UV/vis spectroscopy analysis at a wavelength of 280 nm.

To test the *in vitro* release of the loaded protein from MCM-41 mesoporous silica sheet, the protein-loaded MCM-41 mesoporous silica sheet samples were immersed in pH 7.4 and pH 4.9 PBS solutions, and the supernatant were collected at given time intervals for determining the concentration of BSA by UV/vis spectroscopy.

2.4. Assembly of Ag nanoparticles on MCM-41 mesoporous silica sheet

To assemble Ag nanoparticles on MCM-41 mesoporous silica sheet, 200 mg silica host was soaked into 5 ml $AgNO_3$ (1 wt%) solution for 24 h. After filtered and rinsed thoroughly with deionized water, the product was dried at 60 °C, and then the solid products were treated at 450 °C directly in static air for 1 h to make $AgNO_3$ decompose into Ag.

2.5. Application of the Ag-loaded MCM-41 mesoporous silica sheet for catalytic reduction of 4-nitrophenol

The reduction of the 4-nitrophenol compound by the Ag-loaded MCM-41 mesoporous silica sheet in the presence of $NaBH_4$ was carried out to examine the catalytic activity and reusability of the Ag-loaded MCM-41 mesoporous silica sheet. Typically, an aqueous solution of $NaBH_4$ (2.3×10^{-3} mol L^{-1}) was mixed with an aqueous 4-nitrophenol solution (2.7×10^{-4} mol L^{-1}) in the quartz cell. Then, Ag-loaded MCM-41 mesoporous silica sheet catalysts (0.83×10^{-5} mol L^{-1} relative to Ag nanoparticles) were added to the mixture and quickly placed in the cell holder of the spectrophotometer. The progress of the conversion of 4-nitrophenol to 4-aminophenol was then monitored via UV/vis spectroscopy by recording the time-dependent absorbance spectra of the reaction mixture in a scanning range of 200–600 nm at ambient temperature.

2.6. Characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a JEOL JEM 2010F electron microscope operating at 200 kV. The energy-dispersive X-ray spectroscopic (EDS) measurements were performed with the spectrometer attached on the JEOL-2010F HRTEM. A JASCO V-570 spectrophotometer was used to measure the UV/vis spectra of the nanoparticles at room temperature. Fourier transform infrared spectrometry (FT-IR) was performed on an Excalibur 3100 Fourier transform infrared spectrometer. Small-angle X-ray diffraction (XRD) patterns (RINT2100V/PC, Rigaku, Japan) were determined using Fe-Kα radiation operated at 40 kV and 30 mA. Nitrogen adsorption–desorption measurements were carried out to determine the textural properties of silica materials by using a Quantachrome NOVA 4200e surface area analyzer at −196 °C. The prepared products were dried at 150 °C before analysis. Pore-size distributions were estimated from adsorption branches of the isotherms by using the Barrett–Joyner–Halenda (BJH) method. Pore volumes were determined from the amounts of N_2 adsorbed at the single point of $P/P_0 = 0.98$.

3. Results and discussion

The morphology and structure of the prepared samples were characterized using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). As is shown in Fig. 2, TEM images clearly revealed the hexagonally arrayed nanochannels of MCM-41 sheet. Such micrometer-sized sheets with ordered two-dimensional hexagonal patterns showed that the pore channels are indeed vertical and most of pore diameters are in a size range of 7–8 nm. Under SEM images, the as-synthesized products appear as free-standing sheet form with micrometer dimensions. MCM-41