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Mesocellular polymer foams with unprecedented uniform large mesopores and high surface areas†

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Mesocellular polymer foams with uniform ~17 nm cellular pores were fabricated using mesocellular silica foams as inorganic templates. The mesocellular polymer foams have high surface areas up to ~600 m^2g^{-1} and pore volumes of 1.6 cm^3g^{-1}.

Template synthetic approaches have been extensively applied to synthesize many nanoporous materials.[1–4] Ordered mesoporous carbons have been produced using surfactant templated mesostructured silicas as nano-scale templates.[5] These mesoporous carbons have been successfully utilized as electrodes for supercapacitors[6] and fuel cells.[7] Porous polymer materials have been used as solid-phase supports for organic reactions[8] and chromatographic supports.[9] Recently, several research groups reported on the synthesis of nanostructured polymeric materials using mesoporous silicas as templates. Wu and Bein reported the polymerization of aniline and acrylonitrile within mesoporous MCM-41 silica materials.[10] Linear polyethylene nanofibers were fabricated by extrusion polymerization using titanocene grafted inside mesoporous silica as catalysts.[11] Three-dimensionally interconnected mesoporous polymers were fabricated using silica colloidal crystals as templates.[12] However, the pore size of the porous polymers was macroporous and the surface area was very low. Recently, Yu and coworkers reported the fabrication of ordered mesoporous polymers using ordered mesoporous silica SBA-15 and MCM-48 as the inorganic templates.[13] But the pore size of the ordered mesoporous polymer is below 4 nm. For the extensive applications of porous polymers such as solid-phase supports for organic reactions that require bulky reagents, it is highly demanded to synthesize mesoporous polymers with interconnected large mesopores and high surface areas. Here, we would like to report on the synthesis of mesocellular polymer foams with uniform cellular pores and high surface areas using mesocellular silica foams as templates.

The overall synthetic procedure is described in Fig. 1. Mesocellular silica foam (MCF) was prepared using tetraethylorthosilicate (TEOS) as a silica source, trimethylbenzene (TMB) as a pore expander, and P123 ($(EO)_{20}(PO)_{70}(EO)_{20}$) triblock copolymer as a structure directing agent.[14] By adding an appropriate amount of NH_4F, which was used as polymerization catalyst, into the synthesis gel, MCF with uniform large mesopores was obtained. The calcined MCF was dehydrated at 200 °C under vacuum for 4 hours. A polymer precursor solution composed of divinylbenzene (DVB) and free radical initiator, 2,2′-azobisisobutyronitrile (AIBN) with a molar ratio of 11.5 was wetted into the pores of MCF using incipient wetness method. The amount of DVB was adjusted to 50% of the pore volume of MCF template in order to preserve the cellular structure. Polymerization was performed by heating at 85 °C for 24 hours under an argon atmosphere. Removal of the silica template using 10 wt% HF diluted with ethanol produced mesocellular polymer foam (MCF-P). Prior to sorption analysis of N_2, the samples were evacuated under vacuum until maintaining below 5×10^{-2} Pa at 60 °C. This temperature of pretreatment was chosen to avoid the degradation of polymers in MCF-P. The BET surface area and total pore volume measured at $P/P_o = 0.98$ for MCF silica used as the template for the synthesis of MCF-P were determined to be 555 $m^2\ g^{-1}$ and 1.60 $cm^3\ g^{-1}$, respectively. The nitrogen adsorption–desorption isotherms of the MCF silica with a typical H1 hysteresis loop which are similar to those reported earlier,[14,15] were observed (Fig. S1, ESI†). The isotherms of MCF show a very sharp increase of volume adsorbed at $\sim P/P_o = 0.85$, revealing that the uniform large pore size calculated using BJH (Barrett–Joyner–Halenda) method is centered at ~19.0 nm. The micropore volume of MCF is ~0.06 cm^3g^{-1} determined using t-plot method. This value is well agreed with the results of Kruk *et al.*[15a]

The polymerization process of DVB was monitored by infrared spectroscopy. The CH_2 stretching bending vibrations of poly(divinylbenzene) were observed at 2927 cm^{-1} and 1446 cm^{-1}, respectively (Fig. S2, ESI†). Elemental analysis of MCF-P showed C 89.8 wt%, H 8.1 wt%, and N 1.08 wt%, demonstrating that the silica template was successfully removed by the HF etching. The presence of a small amount of nitrogen appears to originate from AIBN that was used as a free radical initiator for the polymerization of divinylbenzene. The partial filling DVB into the main cells of MCF template can be confirmed by the N_2 isotherms of the poly(DVB)/MCF composite, where the initial mesocellular pore structure of MCF is preserved after DVB wetting and subsequent polymerization (Fig. S3, ESI†). As previously reported, mesoporous silica materials assembled from P123 ($(EO)_{20}(PO)_{70}(EO)_{20}$) triblock copolymer have complementary pores formed from the penetration of ethylene oxide groups into the silica wall.[15] Consequently, some DVB molecules were infiltrated and polymerized in the complementary pores, yielding that poly(DVB) in the main cells was interconnected by the poly(DVB) in the complementary pores.

Fig. 2 shows N_2 isotherms and bimodal pore size distribution derived from the adsorption branch of MCF-P. It is clear that the pore size distribution exhibited two different pores centered around 2.9 and 16.8 nm. The appearance of new small pores could be accredited from the removal of the silica template, which was

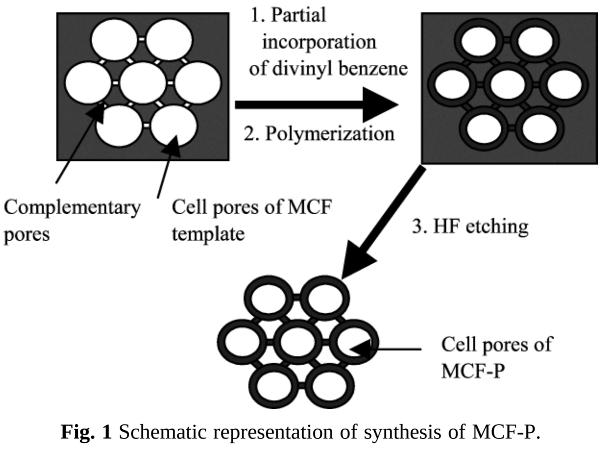

Fig. 1 Schematic representation of synthesis of MCF-P.

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† Electronic supplementary information (ESI) available: isotherms and corresponding pore size distribution of the MCF silica template and poly(DVB)/MCF silica composite, IR spectrum of mesocellular polymer foam, and TEM image of the MCF silica template. See http://www.rsc.org/suppdata/cc/b3/b310713b/

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interconnected with cells and complementary pores. Therefore, the polymer foam possesses small mesopores at 2.9 nm resulting from the replication of the MCF silica wall. The preparation of mesocellular polymer foam having a maximum BET surface area of 600 m^{2}g^{-1} and pore volume of 1.6 cm^{3}g^{-1} was possible by controlling the amount of DVB.

The uniformly sized mesoporous structure of MCF-P is also characterized by transmission electron microscopy (TEM). As shown in Fig. 3, uniformly sized cellular pores in MCF-P are evident in the TEM image. Small mesopores resulting from the dissolution of silica walls of MCF template were not observed, which might stem from the low contrast of polymeric materials.

In conclusion, mesocellular polymer foams with high surface area and pore volume were produced from the selective wetting of DVB into the MCF silica template, followed by polymerization and removal of the template. This MCF-P with bimodal mesopores will find many applications such as catalysis and separation.

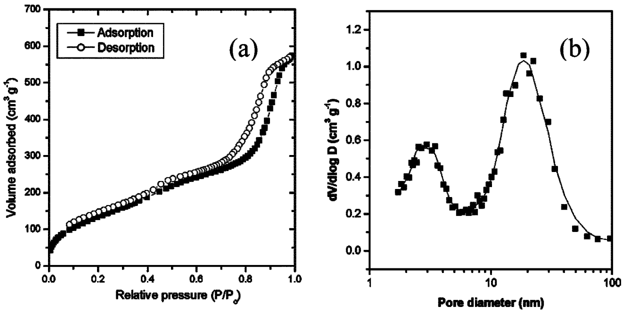

Fig. 2 (a) N_2 adsorption–desorption isotherms of MCF-P and (b) corresponding pore size distribution.

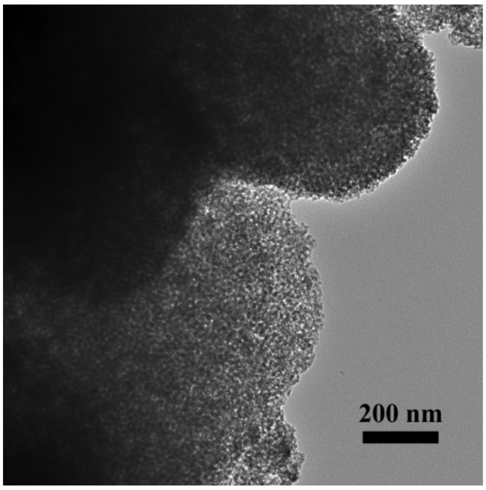

Fig. 3 Transmission electron microscope (TEM) image of MCF-P.

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