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A facile synthesis of bimodal mesoporous silica and its replication for bimodal mesoporous carbon†

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Bimodal mesoporous silica material composed of 30 ~ 40 nm sized nanoparticles with 3.5 nm sized three-dimensionally interconnected mesopores was synthesized under neutral conditions using sodium silicate as a silica source. Using the bimodal mesoporous silica as a template, bimodal mesoporous carbon having 4 nm sized framework mesopores and ~ 30 nm sized textural pores was synthesized.

Since the first synthesis of M41S materials by Mobil researchers in 1992, a tremendous amount of research has been conducted to synthesize various mesoporous inorganic materials using surfactant self-assemblies as templates.[1] In these mesoporous materials, textural pores, along with their main three-dimensional mesopores, are very important because reactant molecules can easily obtain access to the active sites present in framework mesopores. One of the most important research areas in the mesoporous materials is developing an inexpensive and environmentally benign route for the fabrication of three-dimensionally interconnected mesoporous materials containing a large amount of textural mesopores. Recently, our research group and several other groups have synthesized different mesoporous carbon materials using mesoporous silica materials as templates.[2] Because the synthesis of mesoporous carbons involves sacrificing the mesoporous silica templates, the establishment of a low-cost route for producing these mesoporous silica templates would open the way for the cheap production of mesoporous carbons.[2d,2e] Recently, several groups reported the synthesis of bimodal mesoporous silica materials.[3] However, the use of an expensive silica source (TEOS) and the complexity of the synthetic process would hamper the extensive use of these bimodal mesoporous materials. In this communication, we demonstrate the preparation of bimodal mesoporous silica materials by means of a low cost and environmentally benign route. In addition, we synthesized bimodal mesoporous carbon material using the bimodal mesoporous silica as a template. These silica and carbon materials with bimodal mesopores are designated as Meso-nano-S and Meso-nano-C, respectively. Because Meso-nano-S is synthesized under neutral conditions using inexpensive sodium silicate as the silica source, the preparation of Meso-nano-C is also very cost-effective. Although MSU-X type silica materials are known to possess three-dimensionally interconnected wormhole-like pores,[4] there has been no previous report on the fabrication of mesostructured carbon material using MSU-X type silica as a nanometer-scale template. In addition, the current report is the first synthesis of bimodal mesoporous carbon and the first templated synthesis of new mesoporous carbon using the newly developed mesoporous silica template.

Typical synthetic procedure for the Meso-nano-S is as following: 8.6 g of Triton X-114 was dissolved in 200 ml of water containing 4.43 ml of concentrated acetic acid. 16 ml of sodium silicate (Aldrich, 27% SiO_2, 14% NaOH) solution diluted with 200 ml of water was added to the solution with vigorous stirring, and the resulting mixture was heated at 45 °C for 20 h. Then, the mixture was transferred to a polypropylene bottle, and was aged for 20 h at the same temperature under static conditions. The white precipitate was isolated by filtration, dried in air, and was calcined at 550 °C for 4 h to get the final Meso-nano-S

The structure of the mesoporous materials was characterized by X-ray diffraction, nitrogen sorption, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The isotherms of the sample synthesized through the sol–gel reaction at 45 °C without any further hydrothermal treatment shows steep capillary condensation in the range 0.2–0.3 P/P_o, which is typical of mesoporous materials with small pore size (Fig. 1). The absence of additional capillary condensation at a partial pressure of over 0.9 P/P_o, due to the interparticle pores being filled, demonstrates that the pore characteristics of typical MSU-X-type mesoporous silica.[4] In contrast, the mesoporous material synthesized through the hydrothermal treatment at 100 °C exhibits two distinct characteristics in its nitrogen adsorption/desorption isotherms. These are the shift of capillary condensation derived from the framework mesopores to higher relative pressures of 0.6 ~ 0.7 P/P_o and the generation of a new hysteresis curve in the range 0.8 ~ 0.9 P/P_o. The new hysteresis curve observed at high relative pressures is derived from the interparticle pores generated during the hydrothermal treatment at high temperature. The size of the textural mesopores in Meso-nano-S silica material is the smallest among the known mesoporous silica materials, except for the material reported by Coppens and his co-workers.[3c] However, they synthesized the bi-modal mesoporous material using a tedious two step post-synthetic method that required a series of complicated and exhaustive steps. The BET surface area and single point total pore volume of the Meso-nano-S silica are 487 $m^2 g^{-1}$ and 1.07 cc g^{-1}, respectively. The textural pore size of Meso-nano-S was calculated to be 17 nm from the adsorption branch of the

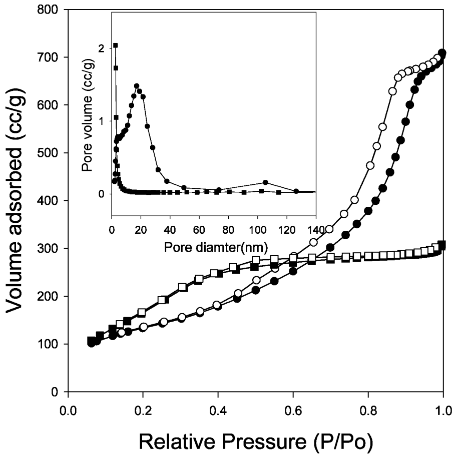

Fig. 1 Nitrogen adsorption/desorption isotherms for the Meso-nano-S (circle) and mesoporous silica synthesized without hydrothermal treatment (square) Inset: Corresponding pore size distributions calculated from BJH (Barrett–Joyner–Halender) theory on the basis of N_2 adsorption data.

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† Electronic supplementary information (ESI) available: experimental procedure and Figs. S1–S4. See http://www.rsc.org/suppdata/cc/b3/b301535a/

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isotherms. The framework pore size, calculated from the desorption branch, is 3.64 nm (Supporting information Fig. S1†). In contrast, the mesoporous material synthesized without the hydrothermal treatment reveals only framework pores of < 2 nm. The XRD pattern of Meso-nano-S silica, revealed a single broad peak at a d-spacing of 5.66 nm, which is a typical pattern for wormhole-like mesoporous materials (Supporting information Fig. S2†).[4,5] The transmission electron microscopic image (TEM) of Meso-nano-S silica (Fig. 2(a)) reveals that the Meso-nano-S silica materials are composed of 30 ~ 40 nm sized particles, having 3 ~ 4 nm sized wormhole-like framework pores. The scanning electron microscopic image (SEM) of Meso-nano-S silica (Fig. 2(a) inset) also revealed that the primary particle size was below 100 nm.

Mesoporous carbons with 3-dimensionally connected pores have been synthesized by our group and other groups.[2a,2b,2h,2i] However, mesoporous carbon having bimodal pores has not previously been reported. Herein, we report on the synthesis of mesoporous carbons having a bimodal pore size distribution, designated as Meso-nano-C, using the Meso-nano-S silica as a template. The synthetic procedure is similar to that reported previously by our group.[2a,2b] But in order to obtain bimodal mesoporous carbon, it is important to control the amount of carbon precursor so that the precursor incorporates only inside the framework pores of Meso-nano-S. The transmission electron microscopic image (TEM) of Meso-nano-C carbon (Fig. 2(b)) showed randomly distributed ~ 4 nm sized framework pores and the SEM image (Fig. 2(b) inset) revealed that the size of the individual carbon particles is less than 100 nm. These TEM and SEM images are very similar to those of Meso-nano-S silica template, which indicates that Meso-nano-S was successfully applied for the template for the synthesis of the bimodal mesoporous carbon.

Fig. 3. show the N_2 adsorption/desorption isotherms and the corresponding pore size distribution of Meso-nano-C carbon, calculated from the adsorption branch by the BJH method. The isotherms exhibited two major capillary condensation steps from the uniform sized framework mesopores and inter-particle connecting mesopores. The pore size generated from the dissolution of the silicate walls was 3.86 nm, which reflects the wall thickness of the Meso-nano-S silica template. Because the classical BJH method systematically underestimates pore size of mesoporous materials, the actual pore size of the Meso-nano-C is larger than 3.86 nm.[6] The fact that the pore size of Meso-nano-C carbon is significantly larger than that of HMS templated carbon[2b] demonstrates that the wall of Meso-nano-S silica is thicker than that of HMS silica.[5] The wall thickness of mesoporous silica is a very important parameter, because thick framework wall will provide a good hydrothermal and mechanical stability.[1b] The average interparticle textural pore size was increased to ~ 30 nm, and the pore size distribution was slightly broadened as compared to the Meso-nano-S silica template. Meso-nano-C also shows only one broad peak in the low-angle XRD pattern (Supporting information Fig. S3†). The surface area and single point total pore volume of Meso-nano-C carbon are 1594 $m^2 g^{-1}$ and 1.80 cc g^{-1}, respectively. As expected, by incorporating excess phenol, mesoporous carbon material having unimodal pore size of 4.2 nm was produced (Supporting information Fig. S4†).

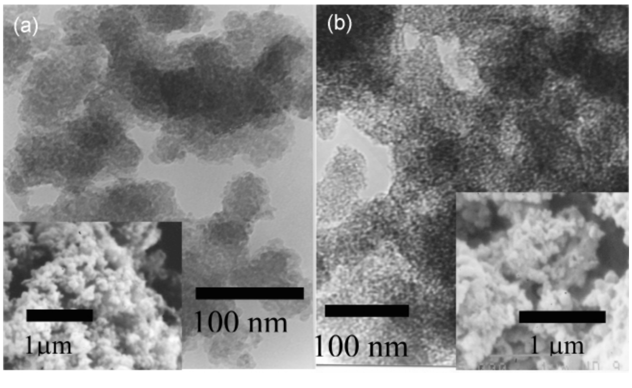

Fig. 2 Transmission electron micrograph (TEM) of (a) Meso-nano-S and (b) Meso-nano-C Inset: Scanning electron microscope (SEM) of Meso-nano-S silica and Meso-nano-C.

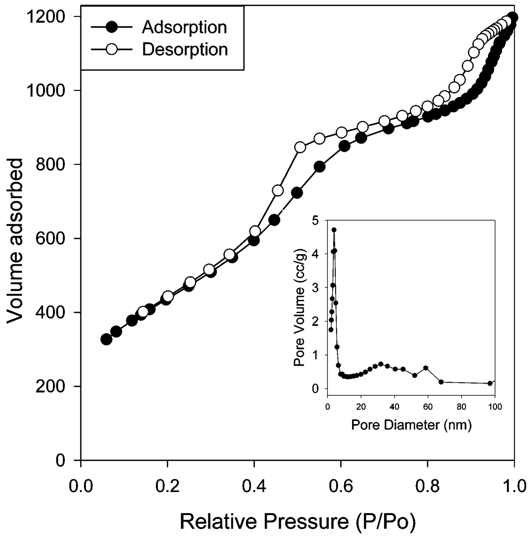

Fig. 3 Nitrogen adsorption/desorption isotherms for the Meso-nano-C carbon. Inset: Corresponding pore size distribution calculated from BJH (Barrett–Joyner–Halender) theory on the basis of N_2 adsorption data.

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