

Formation of monolithic silica gel microhoneycombs (SMHs) using pseudosteady state growth of microstructural ice crystals

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Monolithic silica gel microhoneycombs, which have an array of straight macropores within their structure and developed micro/mesopores inside their walls, were prepared using pseudosteady state growth of ice crystals which occurs during the unidirectional freeze–gelation of freshly gelled aqueous silica hydrogels, followed by a pore-protecting drying method, freeze drying.

Porous materials which are prepared through sol–gel synthesis have been widely used in various fields, such as preparative chromatography, environmental engineering, analytical chemistry, *etc.* The performance of such materials depends not only on their micro/mesoporous properties but also on their macroporous properties.¹ Recently, inorganic porous materials with a hierarchical pore system have attracted considerable attention from the enhanced accessibility to their functional sites, which are distributed on the surface of their micro/mesopores.^{2,3} Such materials with bi/trimodal pore systems are usually prepared through sol–gel synthesis using special templates, such as fine polymer particles and microemulsions. Here we describe a cryochemical synthesis route to prepare monolithic silica gels with bimodal pore systems. In this method, microstructural ice crystals, which can be easily removed by thawing and drying, act as the template.

Cryochemical synthesis methods, such as cryoprecipitation, freeze gelation, freeze casting, and freeze drying, are unique methods which allow the preparation of homogeneous composite materials, biological ceramic composites, porous cryogels with structures similar to aerogels, *etc.*^{4,5} In addition to the nanoscopic superiority of the materials obtained through these methods, cryochemical synthesis enables the production of materials with interesting microscopic features. Thermally induced phase separation which occurs in aqueous colloidal or hydrogel systems results in various types of micromorphology, due to *in situ* ice crystal growth. This phenomenon has been observed in the freezing of various kinds of aqueous sols, gels, and even slurries. For example, quick freezing of such precursors produces a sponge-like micromorphology, which contains three-dimensional interconnected regular/irregular pores inside.^{6,7} Recently, synthesis methods which strategically use ice crystals as templates have attracted considerable attention in the preparation of scaffolds for tissue engineering.^{8,9} Thus, cryochemical synthesis methods are extremely convenient to prepare functional materials with controlled nano/microstructures. Moreover, it is well known that directional ice crystal growth can also produce unique micromorphology.^{10–12} Mahler and Bechtold¹⁰ first showed that the unidirectional freezing of aqueous silicic acid can produce fibers with polygonal cross-sections, mixtures of flakes and honeycombs, or ribbed flakes. Moreover, they also showed that the diameter of each fiber produced using this method is constant along the entire length of the fiber when a thoroughly aged silica hydrogel is unidirectionally frozen under the conditions where pseudosteady state growth of ice crystals occurs. Further studies have been conducted using aqueous slurry systems under non-steady state freezing conditions, and monolithic porous ceramics with irregular but unidirectionally aligned channels have been prepared.¹¹

In this work, we describe a highly reproducible method for the preparation of monolithic silica gel microhoneycombs (SMHs) with unidirectionally aligned homogeneous channels inside them.

Freshly gelled silica hydrogels, in which SiO₂ concentrations are higher than those of Mahler's report, were unidirectionally frozen under conditions where pseudosteady state growth of ice crystals occur. This resulted in the formation of self-constructed and flawless SMHs. Moreover, we combined unidirectional freezing with a pore-protecting drying method, freeze drying,¹³ and obtained SMHs with micropores and mesopores developed inside their honeycomb walls.

Two typical synthesis conditions in this work are shown in Table 1. Commercial sodium silicate solutions (Wako, Japan) were diluted with distilled and deionized water giving solutions of desired SiO₂ concentrations, C_s. Then the pH of the solutions were adjusted to 3 using an ion-exchange resin (Amberlite® IR120B H AG, Organo, Japan). In the case of SMH-2, the pH of the solution was increased again to 8.5 by carefully adding a few droplets of NH₃ *aq* to the solution which was vigorously stirred at 278 K in order not to generate any precipitate. The clear sols obtained were poured into polypropylene tubes, which were 100 mm in length and 10 mm in diameter, and aged at 303 K. Next, freshly gelled hydrogels were unidirectionally frozen by dipping the tubes at a constant rate of v_f into a cold bath maintained at 77 K. It was confirmed that pseudosteady state ice growth initiated at least at about 50 mm from the bottom of the tubes and continued till the tubes were completely frozen, in both cases. Next, the samples were transferred to a cold bath maintained at 243 K and were kept in it for 2 h in order to strengthen their structure in a state where ice crystals act as templates. After this low temperature aging, the parts obtained through pseudosteady state ice growth were cut out and thawed at 323 K. The thawed samples were then immersed into 10 times their volumes of *t*-butanol and were kept there for over 1 day in order to exchange the water included in their structure with *t*-butanol. This washing operation was repeated three times. Next, the wet samples were freeze-dried at 263 K, and finally dry samples maintaining their wet-state nano/microstructures were obtained. The micromorphology of the SMHs were directly observed by a scanning electron microscope (JEOL Japan Inc.; JSM-6340FS). Properties of the pores in the honeycomb walls of SMHs were analyzed from N₂ adsorption–desorption isotherms obtained at 77 K using an adsorption apparatus (BEL Japan Inc.; BELSORP28). Mesopore size distributions were calculated by applying the Dollimore–Heal method to desorption branches of the obtained isotherms.

Fig. 1a shows an overall image of SMH-1, which is a typical SMH obtained by this method. Crack-free monolithic SMHs were obtained. This is one of the benefits of this method, since molding porous materials into the form of monoliths instead of fine powders makes their range of application wider.¹⁴ Note that the overall shape of the SMH, which is a cylinder in this case, depends only on

Table 1 Preparation conditions and physical data of SMHs

Sample	C _s /mol l ⁻¹	t _{gel} ^a /h	t _{hyd} ^b /h	v _f /cm h ⁻¹	S _{BET} /m ² g ⁻¹
SMH-1	1.9	3.4	0.8	6	780
SMH-2	1.6	0.3	1.1	20	691

^a Gelation time at 303 K. ^b Aging time after gelation at 303 K.

the shape of the vessel that is used for preparation. The direction of pseudosteady state ice growth is parallel to the axis of the cylinder. Fig. 1b shows the cross-section of SMH-1. Unidirectionally aligned homogeneous channels can be clearly identified. Fig. 1c is an enlarged micrograph showing the cross-section of channels and wall thickness. This picture indicates that the shape of ice crystals, which were grown under pseudosteady state conditions, was polygonal. This result can be understood by Mahler's explanation which was originally presented for the case of polygonal fiber growth.¹⁰ Although their walls were extremely thin (600 nm) compared with conventional honeycomb supports, the obtained SMHs were not so fragile. This is probably due to the small sizes of their cells (11 μm). The same morphology was observed along the entire length of the SMH-1 sample. Under identical freezing conditions, the thickness of the honeycomb wall tended to become thinner when C_s was decreased. When C_s was decreased to 1 mol l^{-1} , the honeycomb wall started to contain defects, which is thought to be due to the lack of components to build the wall. Fig. 1d shows a vertical section of SMH-1. Straight grown channels can be observed. We also confirmed that the channels ran from one side to the opposite side of the sample by ink penetration tests, which were carried out using red ink dissolved in *t*-butanol.

Besides their unique micromorphology, the SMHs were found to have developed micro/mesopores inside their honeycomb walls. Fig. 2a shows an enlarged SEM image of the honeycomb wall of SMH-2. It can be seen that the honeycomb wall is constructed from numerous colloidal silica particles like typical porous silica gels. Fig. 2b shows the N_2 adsorption-desorption isotherms of the SMHs and the mesopore size distributions estimated from the desorption

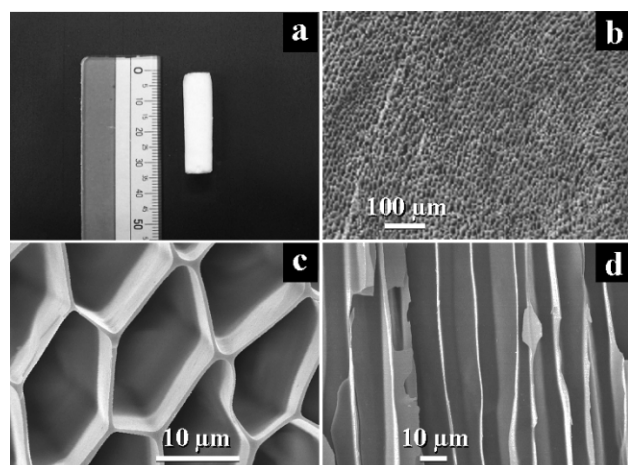


Fig. 1 Morphology and structure of SMH-1; (a) an overall image; SEM images of (b) cross-section, (c) channel structure, (d) vertical section.

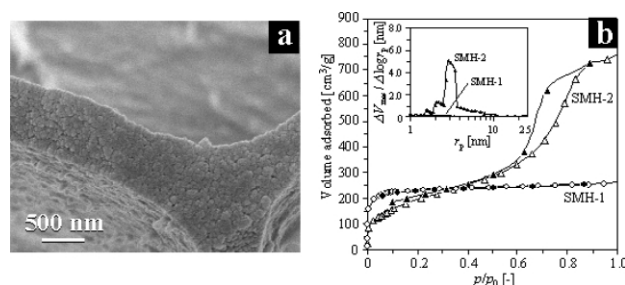


Fig. 2 Nanostructure inside the honeycomb wall; (a) enlarged SEM image of SMH-2; (b) nitrogen adsorption-desorption isotherms. The inset shows the mesopore size distributions from the desorption branches.

isotherms. The N_2 adsorption isotherm of SMH-1 was of type I, which indicates that it is microporous. Its BET surface area, S_{BET} , was calculated to be 780 $\text{m}^2 \text{g}^{-1}$. Interestingly, the N_2 adsorption isotherm of SMH-2 was of type IV, indicating the development of mesopores. This difference in pore size region is thought to be due to the difference in the pH of their parent sols. These results indicate that it is possible to prepare SMHs with different porous properties by unidirectional freeze-gelation of aqueous silicic acid. Moreover, as there is a high possibility of combining this method with conventional techniques for pore size controlling, such as hydrothermal treatment, SMHs with various porous properties can be expected.

In this study, we showed that it is possible to prepare monolithic SMHs by combining pseudosteady state ice growth which occurs during unidirectional freeze-gelation with a pore-protecting drying method, freeze drying. The softness and fairly high SiO_2 concentration of the precursor hydrogel can be regarded as the key factors in this method. When a "soft" precursor is frozen unidirectionally so that pseudosteady state ice growth occurs, an ordered array of independent ice crystals grows within it. This array elongates and effectively acts as a template, and consequently a monolithic gel molded in the form of a microhoneycomb is formed. Considering this mechanism, this method is thought to be applicable to other hydrogels. Though we used a more practical drying method, freeze drying, to preserve the nanoporosity of the hydrogel in this study, it is also possible to use supercritical drying, especially when highly porous gels are desired.

Ordered mesoporous and macroporous solids usually require special templates during their synthesis, which are fairly expensive. Moreover, most of these templates require a special process for their removal, such as chemical treatment or pyrolysis, which could sometimes deteriorate or even destroy the nanostructure of the sample. The proposed "ice-templating" method is completely free from such inefficient processes, since the template "ice" is formed *in situ* and can be easily removed. Therefore, it can be said that this method is not only an excellent method to produce unique monolithic SMHs, but is also extremely practical. As a wide variety of gels having ordered networks of macropores, mesopores and micropores within their structure can be easily obtained, this method is expected to provide new advanced materials for various separation and reaction processes.

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