# Preparation of a self-standing mesoporous carbon membrane with perpendicularly-ordered pore structures

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*Received (in Cambridge, UK) 29th July 2008, Accepted 29th August 2008*
*First published as an Advance Article on the web 1st October 2008*
**DOI: 10.1039/b812982g**

**A self-standing mesoporous carbon membrane (sOMC) with perpendicularly-ordered pore structures was prepared through a simple synthetic method; the pores with a diameter of 8 nm were well ordered over a large area and perpendicularly-oriented to the surface without any external field; in the formation of this ordered structure, the drying process is key, and a porous alumina support is important to induce drying.**

After the development of ordered mesoporous silica,[1–3] many attempts were made to prepare other materials with an ordered mesoporous structure based on the knowledge obtained from studies of mesoporous silica. They seem attractive due to the possibility not only to use them as molecule-selective catalysts based on their size-dependent properties, but also to use them as nanoreactor arrays induced by the ordered nature of the pore structure, since these materials have relatively-large, ordered nanopores (mesopores), with a narrow pore size distribution. In various ordered mesoporous materials, ordered mesoporous carbon (OMC) has potential for catalyst supports, filters, electrodes, separators, sensors, *etc.* due to its large specific surface area, high electroconductivity and physical/chemical durability.[4,5] For example, a catalyst within the pores of OMC has properties such as stabilization of highly-dispersed small catalyst particles,[6,7] and these properties cannot be expected in the case of non-porous supports. Recently, a direct-synthesis method of OMC without using a hard template to induce meso/nanoporous structures, also called soft-template synthesis, has been reported,[8–10] and this method has some advantages against the traditional method using the hard templates. For example, the number of preparation steps and the cost involved in producing these materials can be reduced.

Moreover, the direction of mesopores on the surface is an important factor because the properties of mesoporous materials depend on the ordered nature of the porous structure. The direction of the mesopore structure prepared as a monolith or powder was not generally controlled during preparation. Even in the case of a thin film, the pore structure is known to orient only in a direction parallel to the support.[11] Therefore, it has been an objective to control the pore orientation perpendicular to the surface in a membrane. A lot of studies attempting to orient the direction of pore structure using the interaction between a precursor materials and a support,[12] an external fields[13,14] and meso/micro channels of anodic alumina membranes[15,16] have been published. Among mesoporous carbon materials, membranes with oriented mesopore structure have also been developed.[8,9,17] However, these materials required specific apparatus, expensive surfactants and complicated procedures.

Here, we have attempted to develop a simple preparation method of oriented pore structures using a general apparatus and inexpensive materials. Furthermore, since the applications of mesoporous materials prepared on a support or within a hard template are limited by the properties of supporting materials, we have focused on a self-standing membrane, which is scientifically and technologically important. In this article, we report fabrication of a self-standing mesoporous carbon membrane (sOMC) by using soft-template method. The pores of sOMC were well arranged and the structure was highly perpendicularly-ordered to the surface of sOMC.

Preparation procedure of sOMC was based on the literature.[9] In a typical preparation, resorcinol (1.65 g) was dissolved in a mixture of water (4.35 g)–ethanol (5.75 g)–5 mol dm$^{-3}$ HCl (0.15 cm$^3$). Pluronic® F127 (0.945 g) was further added to this solution, and after its complete dissolution, triethylorthoacetate (1.2 g) and 37% formaldehyde aqueous solution (1.35 g) were added. This mixture was stirred at 30 °C for 20 min, and then a portion of that (carbon precursor) was dropped onto PAM (Whatman Anodisk®, 200 nm pore diameter) in an evaporating dish. The resulting PAM coated with carbon precursors was dried for 15 h in the air at room temperature, and then heated at 105 °C in the oven (KLO-30NH, Koyo Thermo systems Co., Ltd) for 6 hours in order to promote polymerization between resorcinol and formaldehyde. PAM with carbon precursors was further heated at 400 °C in $N_2$ gas flow for 3 hours, and at this moment, the pre-carbonized membrane was removed from the PAM support. Since the interaction between the pre-carbonized membrane and PAM is week, the membrane can be easily removed from PAM. For carbonization, the membrane was heated at 600 °C in Ar gas for 6 hours in the oven (KDF-900, Denken Co., Ltd.). Finally, a shiny black membrane (sOMC) was obtained.

The obtained sOMC had an area of about 25 mm$^2$ and a thickness of about 110 μm. The thickness can be controlled by changing the precursor amount. The membrane had enough strength to be handled by tweezers. sOMC was characterized by FE-SEM. Fig. 1a shows an image of the typical surface of sOMC. The pores seem to be finely aligned on the surface of the membrane. The pore diameter was about 8 nm, and the pore-to-pore distance was *ca.* 14 nm from the SEM observation. The size of the pores is the same as that previously

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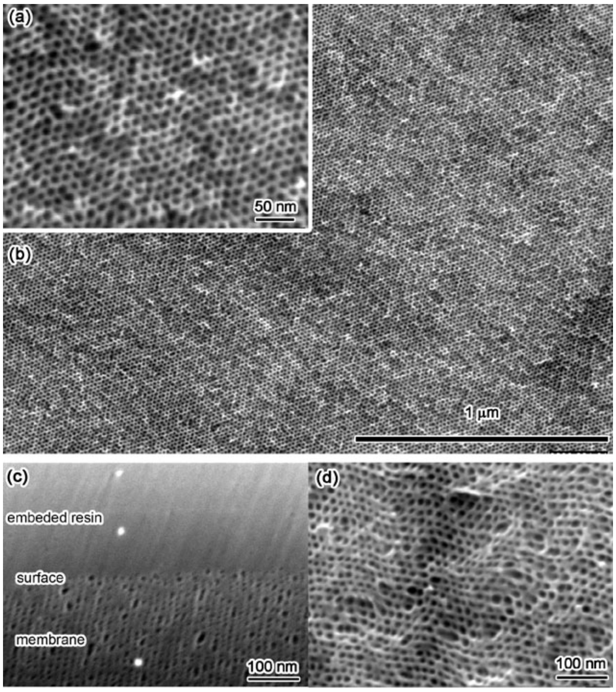

**Fig. 1** FE-SEM images of sOMC: (a) top view with high magnification, (b) top view with low magnification, (c) cross-section view and (d) sOMC without drying process.

reported.[7] A well-ordered mesoporous structure was continuous over a large area of the surface (Fig. 1b). From the cross-sectional view of the membrane (Fig. 1c), perpendicular orientation of pores toward the surface plane was observed, and moreover, nodes were observed within the straight pores. The existing nodes suggest that the pores ordered perpendicular to the surface and in another direction (possibly horizontal to the surface plane) are connected with each other, meaning that the membrane has a 3D-pore structure. To understand the mechanism of formation of well-ordered structures, other experimental conditions (such as without a drying process or with a non-porous alumina support) were tried. In the process without drying, after dropping the precursor on the PAM, it was immediately heated at 105 °C in the oven for 6 hours (for polymerization). Fig. 1d shows a SEM image of the membrane prepared without a drying process, and the degree of orientation of the mesoporous structure appeared to be low. In the case of synthesis with non-porous alumina, an ordered structure was not obtained at all. Therefore, similarly to the fact that a drying process is effective to induce ordered mesoporous structures during the preparation of thin films[17–19] (the synthesis of thick or bulky membranes), the drying process seems to be a key to construct ordered mesoporous structures. Furthermore, the porous support might induce the drying process, and the usage of a porous support is also an important factor to provide ordered mesoporous structures. This is the first achievement in the formation of a self-standing film containing an ordered pore structure without any external field.

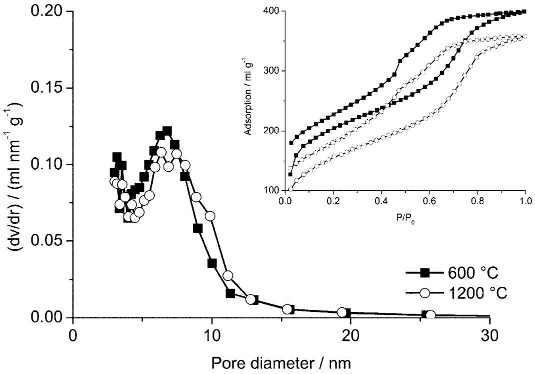

**Fig. 2** Pore size distributions of sOMC obtained using BJH method from $N_2$ adsorption isotherm at 77 K. Open and closed circles show the data of carbonized at 600 and 1200 °C, respectively. The insets show their isotherms.

The BET surface area of sOMC was obtained through $N_2$ adsorption measurement at 77 K, and it was 746 $m^2\ g^{-1}$. The isotherms are represented as filled squares in the inset of Fig. 2. The hysteresis between adsorption and desorption isotherms demonstrates that the membrane has mesoporous structures. The pore size distribution obtained by the Barrett–Joyner–Halenda (BJH) method from the isotherms is shown in Fig. 2. The evaluated diameter of pore is about 8 nm, which corresponds to the result from SEM observations.

Further heat treatment of sOMC up to 1200 °C was performed to obtain highly-carbonized membranes. Based on $N_2$ adsorption measurements at 77 K (open circles in the inset of Fig. 2), the pore structure was retained even after thermal treatment up to 1200 °C under Ar gas flow. Since carbon materials synthesized from polymer precursors, such as phenol, resorcinol, *etc.*, shrink during carbonization, it is difficult to synthesize a mesoporous structured film on a support. However, in our case sOMC was self-standing during carbonization, so the 3D-pore structure still remained, which leads to an advantage in higher conductivity and chemical/physical stabilities.

Structural studies on sOMC were further done by SAXS using Cu K$\alpha$ radiation. The profiles are shown in Fig. 3. Two peaks were observed at $2\theta = 0.655°$ (peak A) and 0.775° (peak B), and *d*-space delivered from these peaks were 13.5 and 11.4 nm,

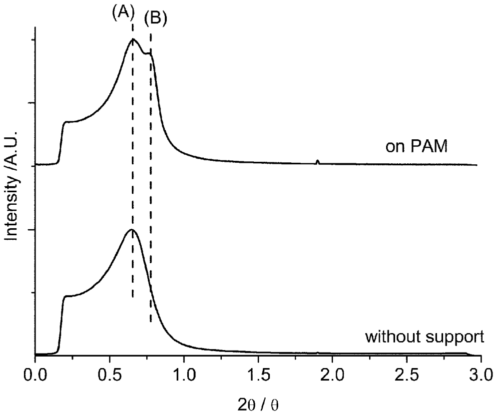

**Fig. 3** Small angle X-ray scattering (SAXS) profiles of sOMC: (top) prepared on PAM, (bottom) prepared without support. The measurements were performed using Cu K$\alpha$ radiation. The $2\theta$ of peak A and B are 0.655° and 0.775°, respectively.

respectively. The *d*-space of 13.5 nm corresponds to the periodicity of the mesopores. Although the precise assignment of the other peak ($2\theta = 0.775^\circ$) requires further measurement, a periodic structure in another direction, which might be a direction horizontal to the surface plane, of 11.4 nm is presumed. This SAXS result also supports an existing 3D-pore structure. In comparison, a SAXS profile of mesoporous carbon prepared without any support shows only one peak at $2\theta = 0.655^\circ$. These results suggest that sOMC has a more highly-ordered structure than that prepared without any support. An exact determination of sOMC's structure cannot be made at the present stage although it may lead to an Im–3m structure based on the literature.[20] Structural studies are still underway.

In conclusion, we successfully prepared a self-standing mesoporous carbon membrane with a perpendicularly-ordered mesoporous structure. We have found that a drying process during the synthesis is significantly related to the ordered nature of the structures, and a porous support is key to inducing that drying process. These novel processes go beyond the previously reported procedures,[9] and it have made feasible the preparation of sOMC. These results could apply to mesoporous carbon membranes with other structures, such as p6m (2D-hexagonal), by changing the ratio of surfactant/carbon source,[20] and furthermore apply to syntheses of other self-assembled materials.

The authors would like to thank the Fuel Cell Promotion Office of Agency of Natural Resources and Energy, Ministry of Economy, Trade and Industry for support. Acknowledgments are also due to the "Development of Technology for Next-Generation Fuel Cells" project of New Energy and Industrial Technology Development Organization (NEDO) for support.

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