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# Hierarchically Porous Carbon Monoliths with High Surface Area from Bridged Poly(silsesquioxane) without Thermal Activation Process

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**Abstract.** Hierarchically porous carbon monoliths with high specific surface areas have been fabricated by removing nano-sized silica phase from carbon/silica composites pyrolyzed from bridged poly(silsesquioxane). This activation method improves the homogeneity between inner and outer parts of the monoliths compared to the conventional thermal activation methods.

## 1. Introduction

Porous carbons have been extensively studied for various applications, including catalyst supports [1], electrochemical devices [2] and gas storage [3,4]. In particular, activated carbons are promising materials due to high specific surface areas arising from the presence of highly-developed microporosity [4,5]. Monolithic porous carbons with high surface area are more manageable for various applications than activated carbon powders because powders need to be fixed or be packed in order to prevent them from being scattered [6,7]. Porous carbon monoliths with high surface areas are usually prepared through an activating process (heat-treatment under a stream of oxidative gas) of precursor monoliths such as carbon aerogels [7,8]. By this method, however, the pore properties of the resultant carbon monoliths include inhomogeneity between inside and outside of the monoliths because the degree of exposure to the oxidative gas is significantly different: the inner parts of the monoliths are less-activated than the outer parts. Another method for developing micropores and increasing surface area of carbon materials is removing silica from carbon/silica nanocomposites [9,10]. This method is believed to be simple and reproducible, but there are also some issues to be improved. For example, small silica particles must be homogeneously dispersed in the carbonaceous matrix to increase the surface area with sharply distributed pore sizes. The other issue comes from the silica/carbon ratios in the composite. When the carbon content is too high in the composites, there would be only a small amount of micropores after removing silica. On the other hand, when the silica content is too high, the surface area of the resultant carbons after removing silica would not effectively increase due to the shrinkage during drying since the carbon skeletons must be mechanically weak. Therefore, only a few are reported on the increase in surface area by this method [9].

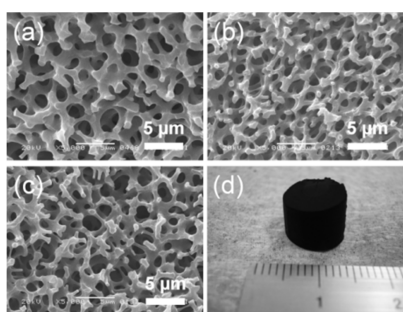
Recently, we have reported that macroporous phenylene- and biphenylene-bridged polysilsesquioxane monoliths can be obtained from the corresponding organoalkoxysilanes by a simple sol-gel method accompanied by spinodal decomposition [11,12]. We have also found that the

hydrothermal treatment of poly(silsesquioxane) networks in a weakly basic solution lead to the mesopore formation through Ostwald ripening. Moreover, both macropores and mesopores were retained even after the heat-treatment in inert atmosphere, resulting in highly porous SiC/C composites above 1400 °C [12].

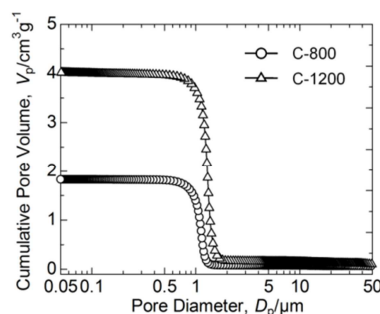
In this study, we have successfully prepared hierarchically porous carbon monoliths with high surface area from the macroporous biphenylene-bridged poly(silsesquioxane) monoliths. The specimens heat-treated under inert atmosphere converted from poly(silsesquioxane) networks to carbon/silica nanocomposites with silicon oxycarbide moieties, in which composite nano-sized silica phases are well-dispersed in the molecular level [10-12]. It is expected that the segregation and growth of the silica-phases are inhibited even at 1200 °C in such composite owing to the surrounding carbons. The subsequent removal of silica from the carbon/silica composites therefore gave rise to the desired hierarchically porous carbon monoliths with uniform porosity and high surface area.

## 2. Experimental

In a typical synthesis, 1.4 g of Pluronic F127 (EO<sub>106</sub>-PO<sub>70</sub>-EO<sub>106</sub>) was dissolved in 8 mL of *N,N*-dimethylacetamide (DMA), and 0.5 mL of 1 M HNO<sub>3</sub> aq. was added. After the complete mixing, 4,4'-bis(triethoxysilyl)-1,1'-biphenyl (BTEBP) was added to the obtained homogeneous solution followed by mixing for 3 min at room temperature. The resultant sol was then stood at 60 °C for 24 h for gelation and aging. The wet gels thus obtained were washed with ethanol (EtOH) followed by the gradual solvent exchange to pure ethanol, EtOH/H<sub>2</sub>O = 9/1, EtOH/H<sub>2</sub>O = 8/2, EtOH/H<sub>2</sub>O = 7/3, EtOH/H<sub>2</sub>O = 6/4, EtOH/H<sub>2</sub>O = 5/5, EtOH/H<sub>2</sub>O = 4/6, EtOH/H<sub>2</sub>O = 3/7, EtOH/H<sub>2</sub>O = 2/8, EtOH/H<sub>2</sub>O = 1/9, and pure H<sub>2</sub>O in this sequence at 60 °C for 8 h each. This solvent exchange process is indispensable to obtain the crack-free monoliths because the monoliths are cracked when the gels are directly immersed in pure H<sub>2</sub>O due to the osmotic pressure. The obtained gels were then hydrothermally treated in 1 M urea aq. at 200 °C for 24 h. The dried gels were obtained after slow evaporative-drying at 40 °C. The dried gels were subsequently heat-treated at 800 °C or 1200 °C for 2 h with a heating rate of 4 °C min<sup>-1</sup> under an argon flow at 1.0 L min<sup>-1</sup>. The resultant carbon/silica composites were immersed in 1 M NaOH aq. at 60 °C for 12 h for three times to remove silica. The obtained carbon monoliths were washed with H<sub>2</sub>O at 60 °C for 4 h for three times followed by drying at 60 °C. The carbon/silica composites are denoted as CS-*x*, while the carbon samples which are obtained after the removal of silica are denoted as C-*x*. Here, *x* represents the heat-treatment temperature.



**Figure 1.** Scanning electron microscopy images of (a) the dried biphenylene-bridged poly(silsesquioxane) precursor gel, (b) CS-1200, and (c) C-1200. (d) Appearance of the carbon monolith (C-1200).

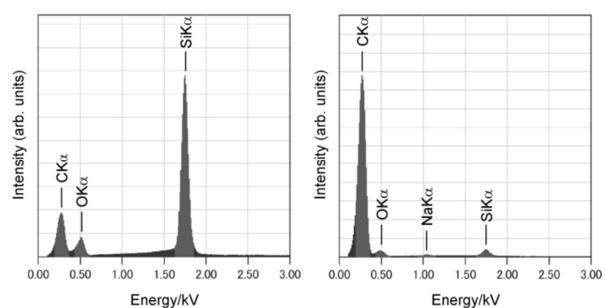


**Figure 2.** Pore size distributions of the carbon monoliths, C-800 and C-1200 obtained by mercury porosimetry.

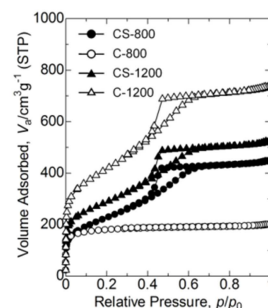
## 3. Results and discussions

Figure 1 (a)-(c) show the macroporous structure of the dried gels, CS-1200, and C-1200

observed by scanning electron microscopy (SEM) (JSM-6060S, JEOL, Japan), while Figure 1 (d) shows the appearance of C-1200. Although the macropores became smaller after the heat-treatment due to the shrinkage during heating, the co-continuous structure is retained. In addition, the macroporous structure did not change by the removal of silica. The monolithic shape is also retained after the removal of silica as shown in Figure 1 (d). The detailed macropore characteristics were investigated by mercury porosimetry (Pore Master 60-GT, Quantachrome Instruments, USA) as shown in Figure 2. It is found that both of the pore size and pore volume of C-1200 are larger than those of C-800. Naturally, a sample heat-treated at higher temperature has the smaller macropores than that heat-treated at lower temperature due to the shrinkage. In this case, however, since CS-800 is mechanically weaker than that of CS-1200, the shrinkage in CS-800 during the removal of silica and the subsequent drying is larger than that in CS-1200. The true density of CS-800 is smaller than that of CS-1200 as shown in Table 1 due to the insufficient densification of the original networks. The higher true density naturally leads to the higher skeletal strength. The pore volume and pore size of C-800 are therefore smaller than that of C-1200 due to the large shrinkage during the silica-removing process.



**Figure 3.** Energy-dispersive X-ray spectroscopy analysis results of CS-1200 and C-1200.



**Figure 4.** Nitrogen adsorption-desorption isotherms of carbon/silica composites heat-treated at 800 °C and 1200 °C and the corresponding carbon monoliths after the removal of silica.

The elemental analysis of the samples before and after the removal of silica was performed with energy dispersive X-ray spectroscopy (EDS) (JSM-6060S, JEOL, Japan) as shown in Figure 3. It is found that the peaks which are attributed to Si and O dramatically decrease while the relative peak height attributed to C increases through the removal of silica. In all samples, the Si/C molar ratio became less than 1% after the removal of silica. The remaining Si are presumably attributed to silicon oxycarbide species which show higher resistance to alkali solution. It is also found that almost all Na from NaOH aq. is removed by washing with distilled water.

The change of the nano-textural properties in the skeletons was characterized by nitrogen physisorption measurements (Belsorp mini II, Bel Japan Inc., Japan) as shown in Figure 4 and Table 1. It is found that the uptake at the very low relative pressure and specific surface area of CS-1200 are larger than that of CS-800, due to the development of micropores in carbonaceous region. In addition, the mesopores were retained in both CS-800 and CS-1200 after the heat-treatment as reported previously [12]. However, the silica-removal process caused the mesopores to collapse in C-800, while the mesopores were retained in C-1200. This can also be explained by the shrinkage during the removal of silica and subsequent drying; the weaker skeletons in C-800 underwent the larger shrinkage as described above. In contrast, the relatively strong carbon skeletons of C-1200 prevented the shrinkage and the mesopores were consequently retained. The specific surface areas increased by the removal of silica in both samples, and the increment is small for the sample heat-treated at 800 °C. In the case of CS-800 and C-800, the large shrinkage during the removal of silica increased the bulk density as shown in Table 1. Although the micropores were tailored by removing silica, only a little increase in specific surface area is

observed due to the drastic increase of bulk density by the shrinkage. On the other hand, in the case of CS-1200 and C-1200, since the stronger skeletons prevented the shrinkage, the bulk density decreased. Both the increase in micropores and the decrease in bulk density caused the large increase in specific surface area.

**Table 1.** Pore characteristics of the samples heat-treated at 800 °C and 1200 °C before and after the removal of silica.

	S <sup>a</sup> /m <sup>2</sup> g <sup>-1</sup>	V <sub>p</sub> <sup>b</sup> /cm <sup>3</sup> g <sup>-1</sup>	True density <sup>c</sup> /g cm <sup>-3</sup>	Bulk density <sup>d</sup> /g cm <sup>-3</sup>	Porosity <sup>e</sup> (%)
CS-800	750	0.692	2.17	0.275	87
C-800	810	0.310	1.75	0.502	71
CS-1200	1060	0.808	2.61	0.315	88
C-1200	1540	1.14	2.12	0.169	92

<sup>a</sup> calculated by the t-plot method. <sup>b</sup> micro- and mesopore volume obtained by nitrogen absorption isotherms at p/p<sub>0</sub> = 0.99. <sup>c</sup> measured by helium pycnometry. <sup>d</sup> measured by mercury porosimetry. <sup>e</sup> calculated as (1 – [bulk density]/[skeletal density]) × 100.

Porosity of the samples was also calculated using the true density and bulk density as shown in Table 1. The true density decreased after the removal of silica in the both samples because of the large weight decrease on the removal. On the other hand, the bulk density of C-800 increased whereas that of C-1200 is decreased, due to the aforementioned shrinkage. The resultant macroporous carbon monolith C-1200 shows remarkably high porosity (92%).

#### 4. Conclusion

In summary, the hierarchically porous carbon monolith with high specific surface area (> 1500 m<sup>2</sup> g<sup>-1</sup>) has been prepared from the poly(silsesquioxane)-derived carbon/silica composite without a thermal activation process. The specific surface area can be largely increased by removing silica at 60 °C from carbon/silica composite which was obtained by heat treatment at 1200 °C. Since the nano-sized silica phases are well-dispersed in the molecular level and the carbon phase inhibits the growth of the silica phase, large increases in microporosity and specific surface area are successfully achieved after the removal of silica. The resultant carbon monolith is expected to have homogeneous pore properties throughout the monolith, which is impossible to obtain by the traditional thermal activation processes in a flow of oxidative gas.

#### References

- [1] Joo S H, Choi S J, Oh I, Kwak J, Liu Z, Terasaki O and Ryoo R 2001 *Nature* **412** 169
- [2] Hu Y S, Adelhalm P, Smarsly B M, Hore S, Antonietti M and Maier J 2007 *Adv. Funct. Mater.* **17** 1873
- [3] Yang Z, Xia Y and Mokaya R 2007 *J. Am. Chem. Soc.* **129** 1673
- [4] Dillon A C and Heben M J 2001 *Appl. Phys. A* **72** 133.
- [5] Shi H 1996 *Electrochim. Acta* **41** 1633
- [6] Lozano-Castelló D, Cazorla-Amorós D, Linares-Solano A and Quinn D F 2002 *Carbon* **15** 2817
- [7] Pröbstle H, Wiener M and Fricke J 2003 *J. Porous Mater.* **10** 213
- [8] Hasegawa G, Kanamori K, Nakanishi K and Hanada T 2010 *Carbon* **48** 1757
- [9] Ye L, Ji Z H, Han W J, Hu J D and Zhao T 2010 *J. Am. Ceram. Soc.* **93** 1156
- [10] Pang J, John V T, Loy D A, Yang Z and Lu Y 2005 *Adv. Mater.* **17** 704
- [11] Hasegawa G, Kanamori K, Nakanishi K and Hanada T 2009 *J. Mater. Chem.* **19** 7716
- [12] Hasegawa G, Kanamori K, Nakanishi K and Hanada T 2010 *Chem. Mater.* **22** 2541