

CARBON-COATED ORDERED MESOPOROUS SILICAS WITH HYDROPHOBICITY AND ELECTRICAL CONDUCTIVITY

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Introduction

Ordered mesoporous carbons can be synthesized by using mesoporous silicas as templates (Ryoo, 1999; Lee, 1999). They inherit high surface area and ordered mesopores from the template silicas. Together with these properties, mesoporous carbons possess some important characteristics such as hydrophobicity and electrical conductivity. It is, however, impossible in principal to prepare mesoporous carbons that have exactly the same structures as the original mesoporous silicas, because of a positive-negative process in the template method. In addition, this mechanism makes it impossible to prepare mesoporous carbons having only 1D mesopores like mesoporous silicas, MCM-41 and FSM-16. Another problem, which would be more serious, is high production costs of the mesoporous carbons. This is due to the use of expensive silica template and the necessity of silica removing process with HF.

If mesoporous silicas can be coated with extremely thin carbon layer such as a single graphene sheet, the resulting mesoporous silicas would acquire hydrophobicity and electrical conductivity with keeping their ordered mesoporous structures almost intact. Such composites can be regarded as the “ordered mesoporous carbons”. Moreover, in this case, the template removal process is not needed, which is very advantageous from the economical point of view. There have been some reports on the production of the mesoporous silicas/carbon composites (Kim, 2003; Zhu, 2004). So far the perfect coating with a single graphene sheet has, however, never been achieved.

Here we report a novel way to uniformly coat mesoporous silica surface with extremely thin carbon layer comprised of only 1 ~ 2 graphene sheets. We demonstrate that such carbon coating endows mesoporous silica with hydrophobicity and electrical conductivity, while its ordered mesoporous structure is preserved.

Experimental

Mesoporous silica, SBA-15, was synthesized according to the method reported previously (Kruk, 2000). In 5 ml of acetone, 2.3 g of 2,3-dihydroxynaphthalene (DN, mp 436 K, TCI, Japan) was dissolved and the solution was poured to 0.47 g of dried SBA-15 in vacuo. The mixture was stirred for several hours at room temperature, followed by the evaporation of acetone at 368 K. The resulting solid mixture of DN and SBA-15 was heat-treated at 573 K for 1 h under a N₂ flow. During this step, liquid state DN was allowed to react with silanol groups (Kamegawa, 1993) on the pore surface of SBA-15 through a dehydration process. Unreacted DN was then washed away with an excess amount of acetone to obtain DN-coated SBA-15. Finally, the coated SBA-15 was heat-treated under a N₂ flow at 1073 K for 4 h to carbonize DN in the silica pores.

Results and discussion

When pure DN was heat-treated up to 1073 K, most of DN evaporated and no residue was left at the final temperature. On the other hand, as much as 64 % of DN was converted to carbon upon the heat-treatment of DN/SBA-15. As a result, 21 wt% of carbon was loaded on SBA-15. The reason for this striking difference would be due to the chemical bonds between DN and silica surface.

Figure 1 shows photographs and electron microphotographs of the original and carbon loaded SBA-15 (carbon/SBA-15) samples. The electron microphotographs were taken by a high-resolution field emission scanning electron microscope (FE-SEM) without spattering. From Fig. 1a and 1b, it is found that the original white silica powder turned black after carbon coating. On the other hand, from Fig. 1c and 1d, it is clearly found that ordered mesopore structure was seen in both samples. The presence of such ordered structure was also

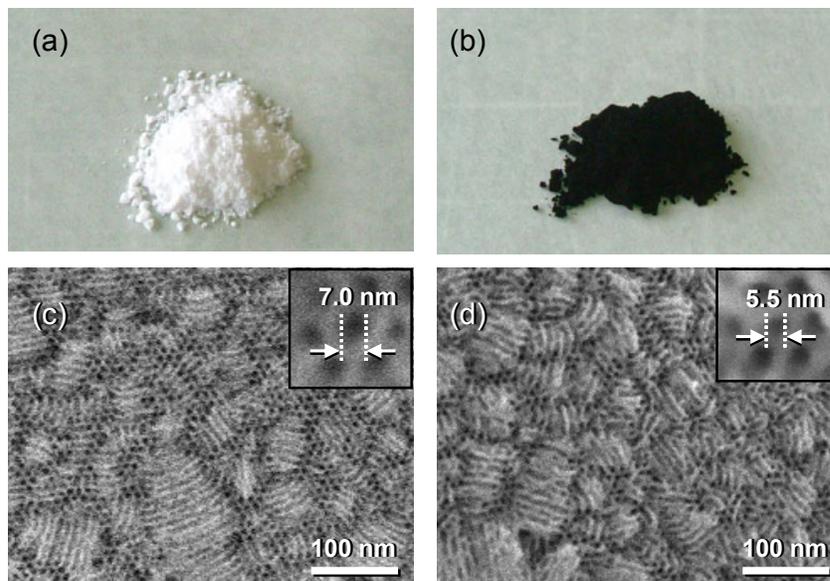


Figure 1. Photographs and high resolution FE-SEM images of a, c) SBA-15 and b, d) carbon/SBA-15. Insets of c, d show enlarged images together with the average mesopore sizes calculated from 150 pores.

confirmed by X-ray diffraction (XRD) patterns. Although the carbon/SBA-15 contains as large as 21 wt% of carbon, we did not observe any carbon deposition on the external surface of the ordered pores. This finding suggests that carbon is uniformly deposited on the inner surface of the SBA-15 mesopores. We measured the diameters of 150 mesopores observed on each of the FE-SEM images (Fig. 1c and 1d) and found that the average mesopore size (5.5 nm) of carbon/SBA-15 was a little smaller than that (7.0 nm) of the original SBA-15. This observation result indicates the uniform carbon coating on the mesopore surface.

Nitrogen adsorption-desorption isotherms for SBA-15, DN/SBA-15 and carbon/SBA-15 are shown in Figure 2, where clear hysteresis loops are observed in the pressure range of 0.4 ~ 0.8, indicating the development of mesoporosity in all samples. The BET surface areas and the total pore volumes are summarized in the second and third columns of Table 1. As expected, these values are decreased when DN or carbon was loaded in the

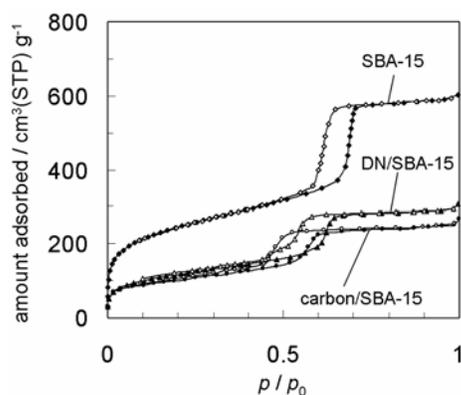


Figure 2. N₂ adsorption-desorption isotherms measured at 77 K.

Table 1. Structural properties of SBA-15, DN/SBA-15 and carbon/SBA-15.

Sample	S_{BET}^a ($\text{cm}^2 \text{g}^{-1}$)	V_t^b ($\text{cm}^3 \text{g}^{-1}$)	d_{DFT}^c (nm)	a^d (nm)	V_w^e ($\text{cm}^3 \text{g}^{-1}$)
SBA-15	830	0.92	6.8	9.99	0.73
DN/SBA-15	410	0.45	6.1	9.90	0.52
carbon/SBA-15	350	0.39	5.3	9.44	0.05

^a BET surface area. ^b Total pore volume calculated from nitrogen isotherm at p/p_0 of 0.96. ^c Mesopore size calculated by the DFT method (available in the Autosorb software) applied to N₂ isotherms. ^d Unit-cell size, which is corresponding to the center to center distance between the cylindrical mesopores. ^e Volume of adsorbed water at p/p_0 of 0.96.

pristine SBA-15. It should be, however, noted that the loaded samples (DN/SBA-15 and carbon/SBA-15) still keep considerable mesoporosity, which accords with the finding that ordered mesopores were microscopically observed on carbon/SBA-15 (Fig. 1). Moreover, the mesopore sizes (fourth column in Table 1) are in good agreement with the corresponding sizes observed in the SEM images (Fig. 1).

As described above, both results from FE-SEM observation and nitrogen physisorption indicate that a thin carbon layer uniformly covers the surface of SBA-15. A thickness of the carbon layer can be estimated from the change in mesopore size upon the carbon coating if change in unit-cell size of the 2D hexagonal ordering is also considered. The unit-cell sizes were calculated from the XRD peak position of (100) diffraction and the calculated values for the three samples are given in the fifth column of Table 1. Due to thermal shrinkage, the unit-cell size decreases with increasing the temperature the sample experienced (573 K for DN/SBA-15 and 1073 K for carbon/SBA-15). Taking into account the decrease in unit-cell size during the heat treatment, we can estimate the pore size of the silica in carbon/SBA-15 to be 6.4 nm. The thickness of the carbon layer can be calculated by subtracting the actual mesopore radius ($d_{\text{DFT}}/2 = 2.65$ nm) from the silica pore radius ($6.4/2 = 3.2$ nm) and the calculated value is 0.55 nm, which is equivalent to the thickness of 1 ~ 2 graphene sheets.

If each mesopore of SBA-15 is completely covered with a single graphene sheet, the graphene would become a single walled carbon nanotube with a diameter of about 6.1 nm, which just fits the pore size (6.4 nm) of the silica in carbon/SBA-15. The presence of such carbon nanotubes in SBA-15 corresponds to a carbon content of about 19 wt%. If a single walled carbon nanotube with a smaller diameter (about 5.4 nm) is further introduced into the already-introduced nanotube in SBA-15, the total carbon content becomes about 30 wt%. The actual carbon content (21 wt%) is in between, suggesting again that the carbon layer is comprised of 1 ~ 2 graphene sheets. To observe the carbon layer with a transmission electron microscope, the carbon part was liberated from carbon/SBA-15 by HF etching, but any tube-like structure was not seen. The carbon layer probably is too thin to keep the tube shape with a diameter of about 6.1 nm, which is much larger than those of typical single walled carbon nanotubes (< 2 nm).

The completeness of the carbon coating is confirmed by the following water vapor adsorption experiment. Figure 3 shows water vapor adsorption isotherms for SBA-15, DN/SBA-15 and carbon/SBA-15. The former two isotherms are characterized by the rapid uptake at a relative pressure of 0.78, because of the capillary filling of water into the mesopores. In these cases, adsorbed water fills more than 80 % of the pore volume (Table 1). In stark contrast, carbon/SBA-15 rarely adsorbs water vapor, revealing its strong hydrophobicity, although the SEM observation and N₂ adsorption experiment clearly indicate the presence of large amounts of mesopores in this sample. It is thus very likely that the pore surface of SBA-15 was perfectly coated with the extremely thin carbon layer.

Since the carbon-coating is almost perfect, the carbon layer is expected to be continuous and carbon/SBA-15 should have electrical conductivity. The conductivity of powdery SBA-15 and carbon/SBA-15 was measured when they are pressed under pressures of around 100 ~ 200 MPa by using an apparatus depicted in Fig. 4a. It was confirmed that SBA-15 has no conductivity, but carbon/SBA-15 is electrically conductive (Fig. 4b). It is thus shown that insulative mesoporous silica acquire electrical conductivity by the carbon coating.

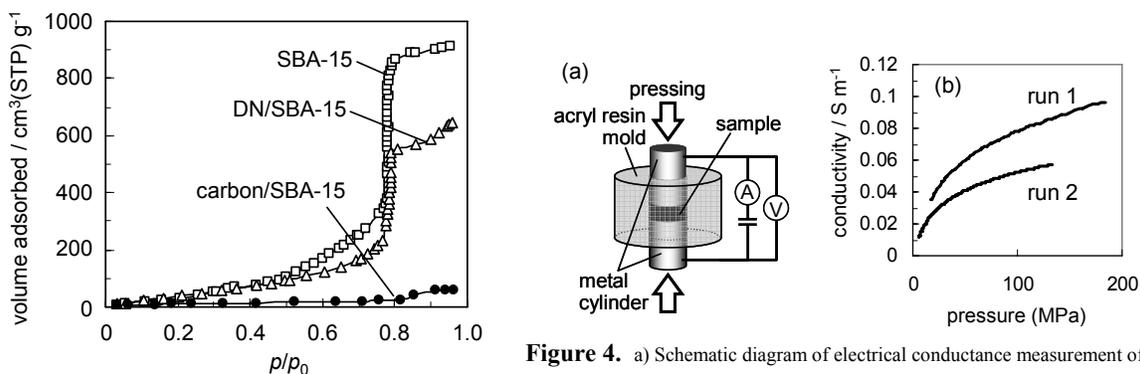


Figure 3. H₂O adsorption isotherms at 298 K for the samples.

Figure 4. a) Schematic diagram of electrical conductance measurement of the samples and b) conductivity versus pressure during pressing the powdery carbon/SBA-15. Conductivity measurement was repeated two times.

Conclusion

In conclusion, mesoporous silica, SBA-15, was uniformly coated with extremely thin carbon layer, which is comprised only 1 ~ 2 graphene sheets. The resulting carbon-nanocoated mesoporous silica still keep the original ordered mesopore structure, but possesses strong hydrophobicity and electrical conductivity, both of which have never been expected in the pristine SBA-15. Since any kinds of mesoporous silicas contain silanol groups on their pore surface, the proposed coating method is applicable to other types of mesoporous silicas. We have actually confirmed the carbon coating for various kinds of mesoporous silicas such as FSM-10, FSM-16, MCM-41, HMS and MSU-H. Moreover, we have used the carbon coated composites with SBA-15, FSM-16, HMS and MSU-H as an electrode of super capacitor in organic electrolyte solution and could observe their electric double-layer capacitance. Thus the present method allows one to use the silicas as the "ordered mesoporous carbons". Furthermore, by using this method, it is possible to uniformly coat even a large size of mesoporous silica such as a membrane. We are now attempting to prepare a large-sized carbon-coated membrane with ordered pore structure.

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