Preparation of Micro-/Macroporous Carbons and Their Gas Sorption Properties

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Received October 2, 2013, Accepted November 5, 2013

Micro-/macroporous carbons (MMCs) were prepared using a hollow mesoporous silica capsule (HMSC) as a sacrificial hard template. The carbonization process after the infiltration of furfuryl alcohol into the template-free HMSC material afforded MMC materials in high yield. The hard template HMSC could be removed by HF etching without deteriorating the structure of MMC. The MMC materials were fully characterized by SEM, TEM, PXRD, XPS, and Raman spectroscopy. The replication processes were so successful that MMCs exhibited a hollow capsular structure with multimodal microporosity. Detailed textural properties of MMC materials were investigated by volumetric N₂ adsorption-desorption analysis at 77 K. To explore the gas sorption abilities of MMCs for other gases, H₂ and CO₂ sorption analyses were also performed at various temperatures. The multimodal MMC materials were found to be good sorbents for both H₂ and CO₂ at low pressure.

Key Words: Porous materials, Microporous carbon, Macroporous carbon, Hydrogen adsorption, Carbon dioxide adsorption

Introduction

Nanoporous carbons have attracted much attention due to their novel characteristics such as high surface area, large pore volume, and high chemical stability. They are being actively developed for their use as better gas adsorbents, catalyst supports for metallic nanoparticles, electrode materials in dye-sensitized solar cells, and high capacity supercapacitors. Meanwhile, several efficient methods for the preparation of hollow carbon capsular materials have been disclosed. Since the first pioneering work by Hyeon and coworkers, Fuertes et al. recently developed a single-step synthetic method of size-tunable hollow carbon capsules based on the Stöber method. Lu et al. also reported dispersible hollow carbon capsules through a so-called confined nanospace pyrolysis method. Despite these successful reports on the preparation of hollow carbon capsular materials, none of the hollow carbon materials produced via these methods has porosity on their carbon shells except the one reported by Hyeon and coworkers. Once the shell has good porosity, the hollow capsular structure would be more favorable for a wide range of advanced applications. Thus, a facile method for the preparation of hollow carbon capsular materials with good porosity in the shell is urgently needed.

Herein, we report a simple preparation method of micro-/macroporous carbons (MMCs) using a hollow mesoporous silica capsule (HMSC) hard template. The sacrificial HMSC materials could be easily prepared by the cholesterol-assisted emulsion technique within a very short period of time. The replication of a siliceous mesostructure into a carbonaceous nanostructure has been well established since the first report for the preparation of mesoporous carbons using a mesoporous silica hard template by Ryoo et al. Nevertheless, the nanocasting of hollow silica spheres into micro-/macroporous carbons has not yet been reported. Micro porous carbons are good adsorbents for small gaseous molecules such as nonpolar H₂ and quadrupolar CO₂. Generally, low-pressure H₂ uptake capacity is directly proportional to the surface area of the adsorbent. It has also been documented that micropore with a large micropore volume is especially good for H₂ uptake at low pressure. In addition, microporous carbon materials are cost-effective CO₂ sorbents for the reduction of greenhouse gases. Therefore, we investigated the gas sorption abilities of MMC materials using H₂ and CO₂ at several different temperatures.

Experimental

Preparation of HMSC-0.50 and HMSC-0.25. 1.0 g of n-hexadecyltrimethylammonium bromide (CTAB, 2.74 mmol), 3.5 mL of 2.0 M NaOH (7.0 mmol), 400 g of H₂O (22.2 mol), and 0.50 g of cholesterol (1.30 mmol) were stirred vigorously at 80 °C for 1 h. Following this, 5 mL of TEOS (22 mmol) was injected at once and heated under reflux for 2 h. After condensation, hot filtration was done and the retrieved solids were washed with H₂O, and then dried at 80 °C overnight. Lastly, the as-made HMSC-0.50 was thermally treated in air at 550 °C for 5 h to remove the template. HMSC-0.25 was prepared using 0.25 g of cholesterol (0.65 mmol) according to the literature.

Preparation of MMC-50. HMSC-0.25 solids (0.10 g) were impregnated with 0.5 M p-toluenesulfonic acid in ethanol (10 mL) for 3 h. After filtration, the solids were dried at 80 °C. The furfuryl alcohol (0.48 mL) was carefully impregnated into the HMSC and dried at 80 °C for 2 h. Carbonization was performed at 800 °C for 2 h under N₂
conditions. The HMSC template was removed by HF etching.

**Preparation of MMC-32.** MMC-32 was prepared through the same method for MMC-50 using HMSC-0.50 solids (0.24 g) and furfuryl alcohol (0.31 mL).

**Physical Measurements.** X-ray diffraction patterns were obtained on a Bruker D8 Advance diffractometer (40 kV, 40 mA). FE-SEM images were recorded on a Hitachi Ultra-High-Resolution Analytical FE-SEM SU-70 (5 kV). TEM analysis was performed on a JEOL JEM-3000F (300 kV). The acetone suspension of the sample was dropped and dried on a Cu grid supported by a holey carbon film for TEM measurements. For ultramicrotoming of the samples, the samples were infiltrated with EPON resin and polymerized at 70 °C for 24 h. Sectioning of the samples was carried out using an ultramicrotome (MT-X, RMC, Tucson, AZ, USA). XPS data were collected on a K-Alpha X-ray photoelectron spectrometer (Thermo VG, UK). X-ray source was a monochromated Al Kα line (hv = 1486.6 eV) and X-ray power was 12 kV and 3 mA. The pass energy of the analyzer for high-resolution spectrum was fixed at 50 eV. The sampling area was 400 μm in diameter. The binding energies were referenced to 284.8 eV (C 1s peak for C–C bonds). Low-pressure hydrogen adsorption measurements were performed at 77 K on a Belsorp-miniII. The equipment was calibrated using Cu-BTC (HKUST-1) as a reference material. Low pressure CO2 adsorption measurements were performed on a Belsorp-miniII at 196 K (2-propanol/dry ice bath), 273 K (ice bath), and 298 K (water bath). All samples were dried at 423 K before gas sorption measurements. Micro Raman measurements were performed in backscattering geometry with a Horiba Jobin Yvon LabRam HR system fitted with a liquid-nitrogen cooled CCD multichannel detector. The spectra were collected under ambient conditions using 514.5 nm line of a He-Ne laser. All MMC materials were exposed with 0.5 mW laser power and 60 s of acquisition time with an area of 1 μm.

**Results and Discussion**

**Characterizations of the Materials.** In order to investigate the effect of the ratio between cholesterol and CTAB on structural variation of HMSC materials, two kinds of HMSC materials, HMSC-0.25 and HMSC-0.50, were synthesized by employing different amounts of cholesterol in the presence of CTAB and tetraethoxysilane (TEOS) in a basic aqueous solution. The corresponding molar ratios of CTAB and cholesterol were 4.2:1 and 2.1:1, respectively. The powder X-ray diffraction (PXRD) pattern of the template-free HMSC-0.25 revealed a well-defined hexagonal diffraction pattern at 2θ = 2.48° (d100 = 3.56 nm), 4.16° (d110 = 2.12 nm), and 4.88° (d200 = 1.81 nm) as depicted in Figure 1. On the other hand, HMSC-0.50 only exhibited a broad diffraction peak at 2θ = 2.17°, d-spacing = 4.07 nm, which was a result from disordered mesostructured silica walls.10 Thus, these results indicated that the mesoscale ordering of CTAB micellar assembly in cholesterol-based emulsion was greatly dependent on the ratio between CTAB and cholesterol under our synthetic conditions.

The morphology of HMSC materials were checked by transmission electron microscopy (TEM, data not shown here) and scanning electron microscopy (SEM) (Figure 2). The hollow spherical shape and the mesostructured wall were maintained as observed before.10 Moreover, a single large hole on the particle surface was discernible from SEM micrographs. Because of this large surface hole, HMSC

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Figure 1. PXRD patterns of HMSC-0.25 (a) and HMSC-0.50 (b).

Figure 2. SEM images of HMSC-0.25 (a) and HMSC-0.50 (b) on the same magnification (× 20,000).
materials turned out to be very efficient protein delivery carriers for intracellular delivery of various large proteins into HeLa cells. Both template-free HMSC-0.25 and HMSC-0.50 exhibited high Brunauer-Emmett-Teller (BET) surface areas of 750 m² g⁻¹ and 719 m² g⁻¹, respectively. The respective pore volumes were 0.61 cm³ g⁻¹ and 0.96 cm³ g⁻¹. As a result, the amount of cholesterol gave a different level of pore volume. The average particle size of HMSC-0.25 is also much larger than that of HMSC-0.50 as depicted in Figure 2. Nevertheless, both materials displayed exactly the same mesopore dimension of 2.43 nm due to the identical structure-directing agent, CTAB.

We also envisioned that the structure of HMSC materials may be adequate as a hard template for other nonsiliceous MMCs. The MMC-based materials were found to be very useful for the development of lithium-ion battery negative electrodes and electrochemical capacitors. The mesopores of HMSC could be efficiently filled with furfuryl alcohol and the resulting aggregated furfuryl alcohol-infiltrated HMSC particles could lead to macroporous texture of carbonaceous material. Thus, two kinds of MMC materials were prepared using HMSC materials as a hard template. Different amounts of furfuryl alcohol were employed as a carbon source in the preparation of MCC-50 and MCC-32. For example, 0.10 g of HMSC-0.25 solid and 0.48 mL of furfuryl alcohol were used to prepare MMC-50. On the other hand, in the preparation of MMC-32, 0.24 g of HMSC-0.50 solid and 0.31 mL of furfuryl alcohol were used. The volumes of furfuryl alcohol corresponded to 50 vol % and 32 vol % with respect to the available total pore volume per gram of the corresponding HMSC-0.25 and HMSC-0.50 hard templates. Therefore, the employed amounts of furfuryl alcohol were excess amounts relative to the available pore volumes of HMSC materials. After the carbonization of furfuryl alcohol-infiltrated HMSCs at 800 °C under N₂, the HMSC template was removed by 48 wt % HF(aq) etching.

The MMC materials were then analyzed by various techniques. Firstly, the structure was investigated by electron microscopic techniques. The SEM images of noncoated samples depicted in Figure 3 revealed that both MMC materials were aggregated spherical particles. The particles apparently resembled the original shape of the HMSC hard template. However, there were significantly distinct features between MMC-50 and MMC-32. MMC-32 exhibited aggregated spherical particles with well-developed surface texture compared with MMC-50. The fibrous surface texture of MMC-32 clearly indicated that the hard templating process was very efficient (Figure 3(b)). Carbon fibers interconnected hollow spheres to lead to macroporous powders. On the contrary, MMC-50 did not seem to have well-developed fibrous surface texture compared with MMC-32. MMC-50 exhibited rather smooth surface texture (Figure 3(a)). Thus, the use of relatively small amount of furfuryl alcohol with respect to the total available pore volume of HMSC hard template would lead to more porous carbon shell with a well-defined surface texture.

The TEM images depicted in Figure 4(a) and 4(b) also
indicate that the templating process was very effective. Both MMC materials exhibited interconnected hollow spherical particles. In order to explore the intact structure in detail, TEM investigation was further performed with ultramicrotommed samples as shown in Figure 5. Most particles were revealed to be aggregated hollow spheres. More importantly, nanostructured textures were clearly discernible for both samples as given in Figure 5(b) and 5(d). These nanoscale surface textures are not real pores but carbon fibers which were generated by filling of carbon precursors into mesopores of HMSC hard templates. The orientation of carbon fibers is parallel to the surface of MMC materials. Apparently, there were no significant structural differences in both samples based on these TEM images. As a result, despite the different surface textures between MMC-50 and MMC-32, the amount of furfuryl alcohol was not so critical for the generation of hollow carbonaceous materials under our synthetic conditions.

The chemical nature of MMC materials was investigated by X-ray photoelectron spectroscopy (XPS) as depicted in Figure 6. Both MMC-50 and MMC-32 displayed mainly carbon species with minor oxygen contents of 4.8% and 4.7%, respectively. A Raman spectroscopic study revealed that both MMC materials exhibited Raman scattering signals which were indicative of graphitic (G) and disordered (D) carbons as shown in Figure 7. Disordering might have resulted from the curved nature of the hollow capsular geometry of MMC materials.\textsuperscript{17,18}

**Gas Sorption Analysis.** \textsuperscript{2} N\textsubscript{2} adsorption-desorption isotherms of the MMC materials measured at 77 K indicated mixed type I and IV isotherms (Figure 8(a)). The adsorption isotherms indicated abrupt increase of adsorbed volumes at relative low pressures that indicates microporosity with small hysteric behaviors at quite high relative pressure that depict some mesoporosity. MMC-50 and MMC-32 exhibited BET surface areas of 493 m\textsuperscript{2} g\textsuperscript{-1} and 693 m\textsuperscript{2} g\textsuperscript{-1}, respectively. MMC-32 exhibited a much higher BET surface area than MMC-50 possibly due to the well-developed fibrous surface texture of the particles. MMC-50 and MMC-32

exhibited total pore volumes of 0.33 cm$^3$ g$^{-1}$ and 0.47 cm$^3$ g$^{-1}$, respectively. Thus, the total pore volumes of MMC materials were directly proportional to the total pore volumes of the employed HMSC hard templates. The MMC materials showed multiple micropore dimensions (Figure 8(b) and 8(c)). Microporosity of porous carbon materials are often beneficial for an efficient uptake of small nonpolar gaseous molecules such as H$_2$ whose kinetic diameter is 2.89 Å. The H$_2$ uptake values at 77 K were 1.13 wt % for MMC-50 and 1.21 wt % for MMC-32 (Figure 9). Interestingly, despite the much lower surface area of MMC-50 than MMC-32, MMC-50 exhibited a very similar level of H$_2$ uptake compared with MMC-32. As previously suggested by Texier-Mandoki et al., low-pressure H$_2$ uptake capacity could also be related to the micropore volume of the adsorbent. The tplot indicated a micropore volume of 0.21 cm$^3$ g$^{-1}$ for MMC-50 and 0.30 cm$^3$ g$^{-1}$ for MMC-32. The external surface area of MMC-50 and MMC-32 were 63.7 m$^2$ g$^{-1}$ and 95.4 m$^2$ g$^{-1}$, respectively. Because the micropore volume and external surface area of MMC-32 are larger than those of MMC-50, the similar range of H$_2$ uptake amounts by both materials may also be affected by other factors. Overall, the H$_2$ uptake values of MMC-50 and MMC-32 were remarkably enhanced than other porous carbon materials that possess much higher BET surface areas than MMC materials. For instance, a series of bimodal mesoporous carbon materials whose surface areas ranged from 961 m$^2$ g$^{-1}$ to 1328 m$^2$ g$^{-1}$ exhibited H$_2$ uptake up to 1.33 wt %. Therefore, the pore textures of MMC materials are likely to be ideal for H$_2$ sorption application.

In the case of CO$_2$ adsorption, MMC-32 exhibited more enhanced CO$_2$ uptake than MMC-50 at 196 K. MMC-32 indicated 203.5 cm$^3$ g$^{-1}$ (9.08 mmol g$^{-1}$) of CO$_2$ uptake while MMC-50 did 158.5 cm$^3$ g$^{-1}$ (6.95 mmol g$^{-1}$). CO$_2$ uptake capacity is likely to be dependent on both BET surface area and pore volumes of MMC materials. The amounts of CO$_2$ uptake were decreased at 273 K and 298 K as follows; MMC-50, 68.5 cm$^3$ g$^{-1}$ (3.05 mmol g$^{-1}$); MMC-32, 72.6 cm$^3$ g$^{-1}$ (3.24 mmol g$^{-1}$) at 273 K and MMC-50, 48.8 cm$^3$ g$^{-1}$ (2.18 mmol g$^{-1}$); and MMC-32, 49.6 cm$^3$ g$^{-1}$ (2.21 mmol g$^{-1}$) at 298 K, as depicted in Figure 10. Nevertheless, the values observed at 298 K and 1 atm for both MMC materials were more enhanced than the previously observed values for other conventional microporous carbon materials such as activated carbon-MAXSORB (0.5 mmol g$^{-1}$) and BPL carbon (0.4 mmol g$^{-1}$) materials under the same conditions. Both materials are often used as benchmark materials for CO$_2$ capture application. Furthermore, the values of MMC materials observed at 298 K were also slightly larger than the previous data of commercially available microporous activated carbon Norit RB2 which exhibited 2.0 mmol g$^{-1}$ CO$_2$ uptake under the same conditions. Considering the fact that Norit RB2 has a BET surface area of 1012 m$^2$ g$^{-1}$ and a pore volume of 0.34 cm$^3$ g$^{-1}$, both MMC-50 and MMC-32 also outperformed Norit RB2 at 298 K. This good performance of CO$_2$ uptake for MMC materials may be attributable to their multiple micropore dimensions and unique hollow geometry.

Conclusion

MMC materials were successfully prepared with HMSC hard templates. The HMSC hard templates could be removed without deteriorating the morphology of MMC materials. This simple nanocasting approach was efficient to prepare nonsiliceous MMC materials. The hollow capsular morphology of template-free MMC materials was confirmed by TEM using ultramicrotomed samples. The MMC materials were microporous with thin shells. The shells were consisted of graphitic and disordered carbon fibers based on SEM images and Raman spectra. These materials were good sorbents for both H$_2$ and CO$_2$ due to their multiple micropore dimensions with hollow capsular geometry. Especially for CO$_2$ capture, MMC materials outperformed several commercial carbonaceous products such as activated carbon-MAXSORB, BPL carbon, and Norit RB2.
Acknowledgments. This work was supported by Hankuk University of Foreign Studies Research Fund of 2013.

References