Graphitic Mesostructured Carbon from an Aliphatic Hydrocarbon Precursor

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Received March 26, 2009, Accepted July 13, 2009

A mesostructured form of carbon was fabricated from a template of mesostructured silica by using pentane, an aliphatic hydrocarbon precursor. To synthesize the mesostructured silica, a buffered (pH of 6.5) mixture of nonionic Pluronic P123 surfactant, sodium silicate, and acetic acid were used. The impregnated silica with $Fe(CO)_5$ (wt 5%) and pentane was placed in a quartz tube, treated with pentane vapor at 800 °C for two hours to synthesize the mesostructured carbon. The XRD patterns of the carbon replica in the low/wide angle regions, its TEM images, and nitrogen adsorption-desorption isotherm revealed that the long-range framework order of mesostructure with the pore size centered on 2.8 nm was maintained to some extent mainly due to some portions of mesophase carbon that work as a support to fix the hexagonal frameworks by anchoring on the pore surface with an improved graphitic character. The dc conductivity of the mesostructured carbon in pressed powder form at 6.0 MPa was 2.08 S/cm.

Key Words: Graphitic mesostructured carbon, DC conductivity, Mesostructured silica template, Pyrolysis of pentane, $Fe(CO)_5$

Introduction

Porous carbon nanostructures have been widely studied for adsorption, catalyst supporter, and energy storage.[1,2] Especially, if the carbon is in graphitic form, the electronic property, corrosion resistance, and surface property make the material useful for electrical applications.[2,3,4] Recently, the high surface area and porosity of carbons could be formed through the replication of mesostructured silicas. In this article 'mesostructured' means mesporous with pore regularity. The hexagonal silica mesostructure known as SBA-15 and its cross-linked analog MSU-H have been attractive templates for carbon replication because their framework walls are comparatively thick and they have abundant micropores interconnecting each other.[5,6] Sucrose has been the most commonly used precursor for the fabrication of mesostructured carbons.[7] However, the resulting carbon has little graphitic character because the synthesis of such mesostructured carbon with ordered pores was possible with an amorphous carbon character. A few years ago, through SBA-15 template, a mesostructured carbon replica with graphitic character was synthesized from acenaphthene as the precursor under an autoclave condition.[8] With the MSU-H silica template, different mesostuructured carbon replicas of graphitic character were produced by the author from aromatic precursors, benzene, naphthalene, anthracene, and pyrene without the need for autoclave.[9]

In this work an aliphatic precursor, pentane, in combination with $Fe(CO)_5$ as a catalyst, was used to obtain a mesostructured carbon replica having a graphitic character. Previous reports have implied that $Fe(CO)_5$ is a useful metal source for the synthesis of carbon nanotubes with pentane as a carbon source but have not tried out for the preparation of mesostructured carbon network.[10,11,12]

Experimental Section

Mesostructured silica template, MSU-H, was prepared as described before[6] from a mixture of Pluronic P123 surfactant ($EO_{20}PO_{70}EO_{20}$) as the structure-directing material, sodium silicate as the silica source, and sodium sulfate as a mineralizer to obtain a more rigid silica framework. The mixture of P123 1.0 g in H_2O 10 mL and 1 M acetic acid 10 mL was stirred for 1 hour, and the solution of sodium sulfate 0.86 g in H_2O 10 mL, and then the solution of sodium silicate 2.7 g in H_2O 20 mL were added, stirring the mixture. The buffered condition with acetic acid was maintained at pH 6.5. The mixture was allowed to react at 60 °C in shaking water bath for 24 hours. It is then filtered with the salt being washed out, and calcined at 550 °C for 6 hours to remove the surfactant. The mesostructured phase of silica product was confirmed by X-ray diffraction.

For the synthesis of carbon replica from the pentane precursor, $Fe(CO)_5$ (0.25 g) as a catalyst was dropped into nitrogen-filled pentane (4.75 g) and the dried silica template (1.0 g) was impregnated with the solution. The impregnated silica was compacted into a quartz tube. The suspension was purged with nitrogen, and then carbonized at 800 °C for 2 hours under a flow of nitrogen, which was saturated with pentane vapor. For the reaction, U-shaped tube was filled with pentane. The nitrogen gas flew from one side of the U-tube and passed through it resulting in bubbling of pentane. The nitrogen gas and pentane vapor emitted from the other side of the U-tube flew continuously into the quartz tube containing the impregnated silica in a tube furnace. The resulting carbon-mesostructured silica composite was suspended in 25% HF overnight to remove the silica template. The traces of iron produced by decomposition of $Fe(CO)_5$ were checked out through X-ray analysis whether iron disappeared completely after the process.

From the powder X-ray diffraction patterns of the carbon replica in the low- and wide-angle regions, the hexagonal framework order of the mesostructured carbon and the graphitic character were investigated. In order to get the image of the mesostructured carbon replica, TEM (transmission electron microscopy, JEOL Corp.-JEM2100F) was used. For the textural

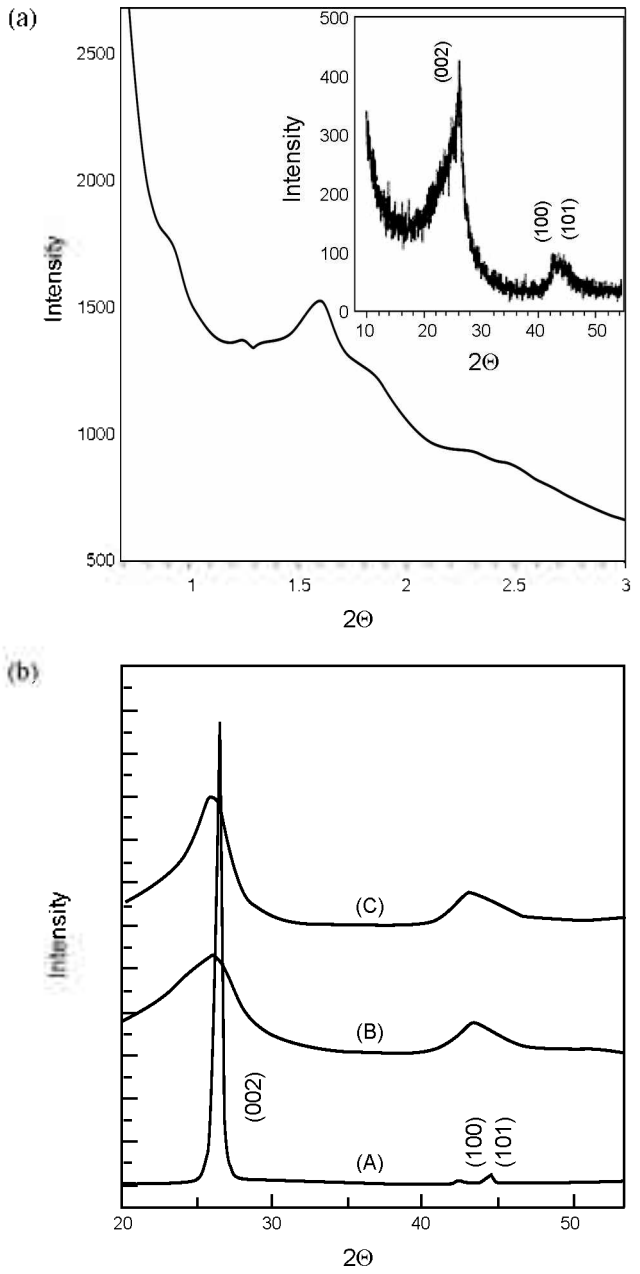

Figure 1. (a) XRD patterns of carbon replica prepared from pentane in the low-angle region and in the wide-angle region. (b) XRD patterns of graphite powders, A) raw; B) ball-milled for 24 hrs; C) ball-milled for 24 hrs and then annealed at 1700 °C for 9 hrs.[13]

property measurement of the mesostructured carbon, the carbon replica was evacuated overnight at room temperature and the nitrogen adsorption-desorption isotherms were applied at −196 °C on a Micrometrics Tristar instrument. The dc conductivity of the carbon replica was determined by using Keithley 236 source unit and four-probe method at an applied current of 10 mA and an applied voltage of 1.0 V after pressing the carbon powder into a quartz glass tube at 6.0 MPa.

Results and Discussion

Figure 1(a) shows the powder X-ray diffraction patterns for

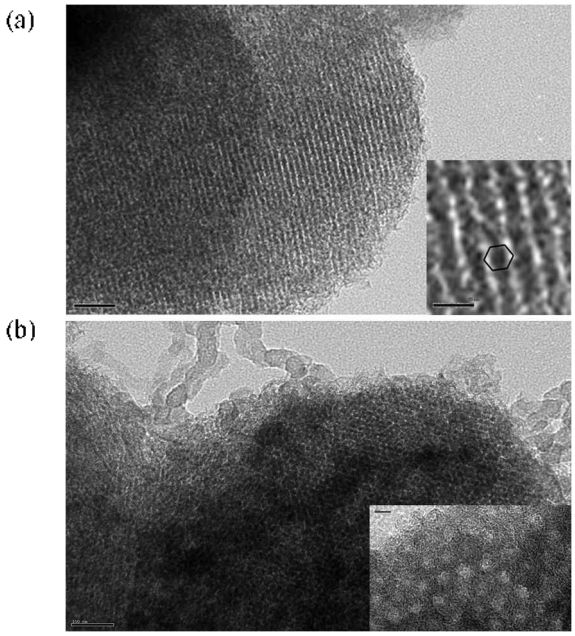

Figure 2. (a) TEM image of mesostructured carbon replica from pentane source at magnifications with the scale size of 100 nm. The enlarged scale size is 25 nm. (b) TEM images of carbon replica with the scale size of 100 nm and the inset scale size of 20 nm.

the mesostructured carbon in the low- and wide-angle regions. Although the low angle XRD pattern of the carbon replica revealed a lower long-range framework order, compared with the hexagonal framework order of silica template[6] and carbon replica prepared by sucrose,[7] it had a greater graphitic structure, as indicated by the intensity and line widths of the wide angle pattern. The X-ray pattern shows a peak centered at 2 θ = 26°, which is similar to the (002) diffraction of the graphite structure. However, somewhat broad X-ray pattern at around 2 θ = 26° and 43 ~ 45° in the wide-angle region corresponding to the (002) and (100)/(101) diffractions is found indicating that the liquid-like mesophase still exists and the mesophase contributes to form a hexagonal framework order. Sucrose as a carbon precursor has been reported to show a very broad pattern in the wide angle Bragg reflections, especially at (002) diffraction of graphite,[9] which produces an excellent hexagonal carbon replica. As a reference, Figure 1(b) shows the X-ray patterns of the raw and the processed graphite powders.[13]

The TEM image of the carbon replica from pentane source shows excellent ordering of the hexagonal network arrays, approximately 10 nm carbon rod-like in diameter and 3 nm apart in Figure 2(a). The rod-like carbon represents the replica of consecutive hexagonal framework order of the template. Interestingly, the TEM image in Figure 2(b) also describes the highly ordered framework arrays. The discoid alignment, which is shown in the inserted picture within Figure 2(b), is related to the anchoring of aliphatic hydrocarbons in liquid-like mesophase on surface of the silica template during carbonization. Thus aliphatic hydrocarbon in liquid-like mesophase works as a support in maintaining the hexagonal mesoporous frameworks by anchoring on the pore surface. The anchoring nature of the carbon on pore surfaces would be a useful property for the future appli-

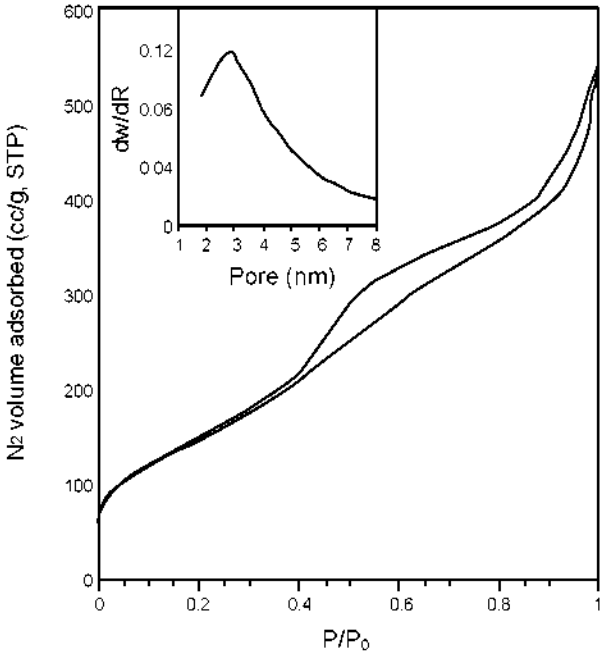

Figure 3. Nitrogen adsorption-desorption isotherm of carbon replica from the pentane precursor. The insert provides the BJH pore size (nm) distribution calculated from the N_2 isotherm.

cations as a support in fabricating long-range porous clusters. As confirmed in X-ray pattern and TEM images, no trace of iron was found indicating that after $Fe(CO)_5$ and the pentane precursor were decomposed during the carbonization process at 800 °C, the possible iron trace was dissolved out by 25% HF treatment. The boiling points of $Fe(CO)_5$ and pentane are 102.8 °C and 36.1 °C.

Figure 3 shows nitrogen adsorption-desorption isotherms for the carbon replica with the BET surface area (578 $m^2 g^{-1}$), pore volume (0.78 $cm^3 g^{-1}$), and pore size (2.8 nm). The isotherm curvature elucidates that the mesopores possess non-rigid slit-shaped pores.[14] The adsorption proceeds on the pore surfaces until p/p_0 is reached to unit due to delayed capillary condensation. Once the condensation has occurred, the state of the adsorbate is changed and desorption curve follows a different path even though the mesopores are slit-shaped.[14] Although the mesostructured carbon replica shows quite low hexagonal order in XRD low-angle region and does not exhibit a well-defined step in the nitrogen isotherm. TEM images and the property of pore size centered on 2.8 nm indicate that it is possible to synthesize a mesostructured carbon replica by using the mesostructured silica template and an aliphatic hydrocarbon source.

The dc conductivity of the mesostructured carbon replica for powders pressed at 6.0 MPa was 2.08 S/cm, larger than the conductivity of carbon replica formed from sucrose, 0.0016 S/cm.[9] It is clear that the electrical conductivity of a mesostructured carbon can be increased by improving its graphitic character.

Conclusion

The above results imply that the formation of improved graphitic framework containing regular pores can be conveniently prepared at ambient pressure with an aliphatic hydrocarbon precursor and proper catalyst if the small portion of liquid-like mesophase sticking on the template surface works as a support to fix the mesostructural framework. Mesostructured carbon replica with graphitic character would be very useful for the future electrochemical applications, such as fuel cells, electrochemical sensing materials, and fabricating various functional materials intercalated into/on the graphitic framework.

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