Novel Hexagonally Ordered Nitrogen-doped Mesoporous Carbon from SBA-15/Polyaniline Nanocomposite

Ajayan Vinu,*[1] Pavuluri Srinivasu,[1] Toshiyuki Mori,[1] Toshio Sasaki,[2] Anjana Asthana,[2]
Katsuhiko Ariga,[3] and Shunichi Hishita[2]
[1]*Nano-ionics Materials Group, Fuel Cell Materials Center, National Institute for Materials Science, Tsukuba 305-0044*
[2]*Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba 305-0044*
[3]*Supermolecules Group, National Institute for Materials Science, Tsukuba 305-0044*

(Received March 19, 2007; CL-070285; E-mail: vinu.ajayan@nims.go.jp)

A novel nitrogen-doped mesoporous carbon with well-ordered two-dimensional (2D) structure has been successfully prepared for the first time using aniline as a source for both carbon and nitrogen, and SBA-15 as a template. The above material has been unambiguously characterized by various sophisticated techniques such as XRD, HRTEM, XPS, and nitrogen adsorption. The obtained material possesses very high surface area, pore volume, and uniform pore size distribution. The XPS and CHN analysis revealed that nitrogen atom is successfully doped on the mesoporous carbon walls.

The fabrication of well-ordered mesoporous carbon materials with different structure types using mesoporous silicas with 2D and three-dimensional (3D) structures as the nanotemplates has received much attention. The physicochemical properties of these carbons, such as high surface area, pore volume, ordered pore structure, and chemical inertness make them promising candidates for a variety of applications, including the size and shape selective adsorption, separation, catalysis, immobilization of biomolecules, electrochemistry, and biomedical engineering (see several articles and references therein).[1–6] The introduction of foreign atoms into the carbon nanostructures has received much attention because it can enhance the mechanical, conducting, field emission, energy storage, and the surface properties of the materials.[7–9] Recently, Sharma et al. fabricated the B- and N-doped carbon nanotubes and reported that the field emission properties of carbon can be easily controlled by varying the amount of N-doping.[8] Paez et al. also found that the concentration of reactive points in carbon nanotube wall increases with increasing the doping atoms, thus causing clear electronic and structural differences.[9]

Ordered porous carbon materials doped with foreign atoms are expected to play an important role in controlling their semiconducting properties.[7–10] Kyotani et al. reported that N-doped microporous carbon can be produced using zeolite Y which exhibits the faujasite structure with 3D pores, furfuryl alcohol and acetonitrile as the template, carbon and nitrogen sources, respectively.[10] Unfortunately, they are microporous in nature, thus they can not be used for the immobilization of large heme proteins which is critical for the biosensing application. N-doped carbon materials with mesoporous structure can offer many distinct advantages not only for biosensors for which the adsorption of large size heme proteins on the porous matrix is required to enhance the protein stability and electron transports or catalytic transformation of bulky molecule but also for other applications such as energy storage and fuel cells. Very recently, Vinu et al. have prepared mesoporous carbon nitride with very high surface area, pore volume and well-ordered porous structure through the polymerization reaction between ethylenediamine and carbon tetrachloride using SBA-15 as the template.[11] We have also synthesized mesoporous BN and BCN by novel elemental substitution technique using mesoporous carbon as the template.[12] However, the research on the mesoporous carbon materials "doped" with foreign atoms is quite limited. In this communication, we report for the first time on the synthesis of well-ordered nitrogen-doped 2D mesoporous carbon material using SBA-15 as the template and aniline as the precursor for both carbon and nitrogen. The above material has been thoroughly characterized by various sophisticated techniques such as XRD, HRTEM, XPS, and nitrogen adsorption measurements. It has been found that the nitrogen atom has been successfully doped on the walls of the mesoporous carbon material.

In a typical synthesis of N-doped mesoporous carbon, 0.5 g of calcined SBA-15[13] was thoroughly mixed with 2.5 g of aniline. The polymerization of aniline inside the nanochannels was done by adding 3.5 g of ammonium peroxydisulfate ($NH_4S_2O_8$, APDS), and the resultant greenish black mixture was heated at 100 °C for overnight. Then, 3.0 g of APDS was again added to the obtained greenish solid mixture to get the complete polymerization and dried in a vacuum oven at room temperature for 24 h. The resultant black colored SBA-15/polyaniline nanocomposite was ground into a fine powder and carbonized at 900 °C in a nitrogen flow of 100 $mL\,min^{-1}$ with a heating rate of 3.0 $°C\,min^{-1}$ and kept under these conditions for 5 h. The material was recovered after dissolution of the silica framework in 5 wt % hydrofluoric acid, followed by filtration, washing several times with ethanol, and drying at 100 °C. The obtained material was designated N-MCPA.

Figure 1 shows the powder XRD diffraction patterns of N-MCPA along with the parent mesoporous silica template, SBA-15. N-MCPA exhibits three well-resolved peaks, which can be assigned to (100), (110), and (200) reflections of 2D hexagonal lattice (space group *p*6*mm*), similar to the XRD pattern of parent mesoporous silica template SBA-15 which consists of the hexagonal arrangement of well-ordered cylindrical pores and the pores are interlinked by the micropores present in the walls.[13] Figure 1, inset A and B show the high-resolution transmission electron microscopic images of N-MCPA with low and high magnifications, respectively. The sample exhibits a highly ordered mesoporous structure with linear array of mesopores separated by the nitrogen-doped carbon walls, originating from the mesoporous silica framework that would convert into the mesopores of the resultant carbon after the HF treatment. It should be mentioned that the structural features and the morphology of the N-MCPA are almost similar to those of the parent silica template, SBA-15.[13]

Nitrogen adsorption–desorption isotherms of N-MCPA in comparison with the parent silica template are shown in Figure 2. Both the samples exhibit type IV adsorption isotherm

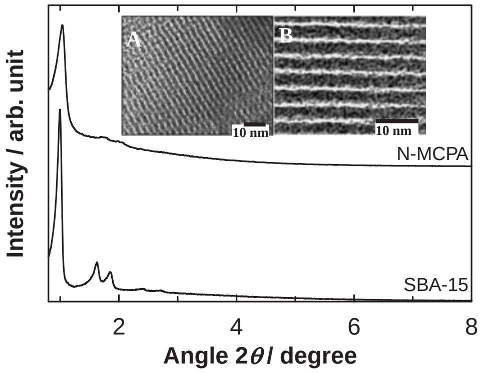

Figure 1. Powder XRD patterns of N-MCPA and SBA-15. XRD patterns were recorded on a Rigaku machine using $\mathrm{Cu}\,K\alpha$ radiation in the range of 0.8 to 10° with the 2θ step size of 0.01° and a step time of 1 s. HRTEM images were obtained with JEOL JEM-2000EX2.

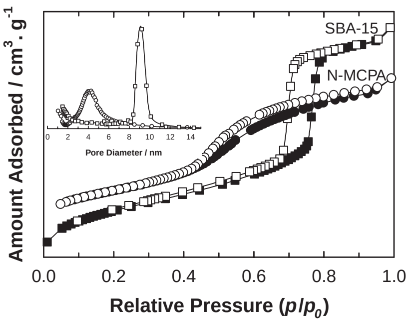

Figure 2. Nitrogen adsorption–desorption isotherms (adsorption: closed symbols; desorption: open symbols) and (inset) Barret–Joyner–Halenda (BJH) pore size distributions of N-MCPA and SBA-15: (■) SBA-15 and (●) N-MCPA.

with a sharp capillary condensation step, which is typically observed for the well-ordered mesoporous materials. The surface area and the specific pore volume of N-MCPA is found to be $1064\,\mathrm{m^2/g}$, and $1.01\,\mathrm{cm^3/g}$, respectively. The BJH pore size distribution data calculated from the adsorption branch of the nitrogen adsorption isotherm reveals that the pores are highly uniform with the average size of 4.3 nm (Figure 2, inset).

The CHN analysis confirmed the presence of nitrogen in N-MCPA. The overall carbon to nitrogen ratio is found to be 15. The XPS analysis also confirmed that the material is mainly composed of carbon and nitrogen with small amount of sulphur and oxygen (Figure 3a). The small percentage of S and O come from the oxidising agent and the moisture and/or ethanol, respectively. The XPS C1s spectra could be deconvoluted into two peaks with binding energies of 283.6 and 284.5 eV. The peak at 283.6 can be attributed to pure sp^2 carbon atoms in the graphitic site of nitrogen-doped amorphous carbon matrix while the peak at the highest energy 284.5 eV is assigned to the sp^2 carbon atom bonded with nitrogen.[7,11,14] Figure 3b shows the N1s core level spectrum of N-MCPA. The fitting of the peak shows the existence of three contributions with the binding energies of 397.4, 400.2, and 403.9 eV. These peaks can be assigned to nitrogen sp^2 bonded to carbon, nitrogen atoms trigonally bonded to all sp^2 carbon atoms, and oxidized nitrogen, respectively.[10,11,14] It is interesting to see that the amount of nitrogen atoms trigonally bonded to carbon atoms is much higher as compared to that of other form of nitrogen environment. These results confirmed that the aniline molecules have been successfully transformed into nitrogen species through the condensation reactions occurring during the carbonization process at very high temperature.

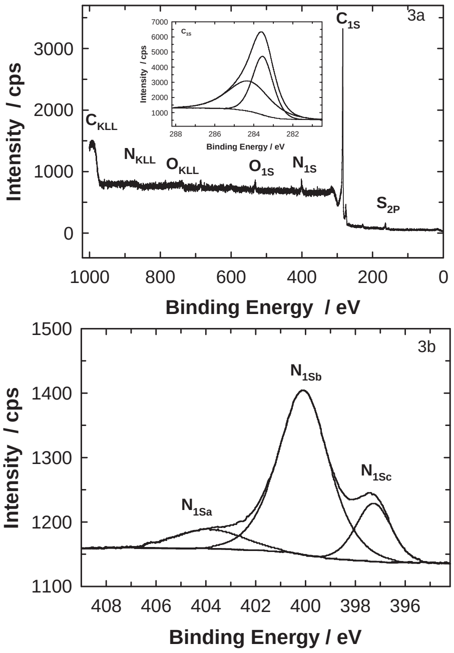

Figure 3. (a) XPS survey, (b) N1s, and (inset) C1s spectra of N-MCPA. Calibration was done by using the O1s peak (531 eV).

In conclusion, a novel hexagonally ordered nitrogen-doped mesoporous carbon was obtained for the first time using aniline as the source for both carbon and nitrogen, and SBA-15 as the template. The aniline molecule was successfully polymerized inside the channels of mesoporous silica with APDS. The XRD, HRTEM images, and the nitrogen adsorption data revealed that the material possesses well-ordered pore structure, high surface area, uniform pore size distribution, and high specific pore volume. The XPS results revealed that the nitrogen atoms are successfully doped inside the carbon walls and are trigonally bonded to graphitic carbon atoms. We strongly believe that the material could be useful for various applications, such as catalytic supports, gas storage, and sensors.

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