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NOVEL CARBON STRUCTURE PREPARED USING MICA AS TEMPLATE

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A fluorine expandable mica (EM), having two-dimensional spread in its crystal form, was used as a template for carbonization of organic liquids such as quinoline and pyridine. Despite Intrinsic volatile under the ambient pressure, these organic liquids inserted into the interlayer space of mica yielded carbonaceous compound after heat treatment over 500°C in inert atmosphere. The particle size of the compound separated from the mica layer depends on that of mica as a template. Detailed TEM observation revealed unique structure, namely each particle comprised two structural parts: film and surrounding rim part. The film part was very thin, thus being transparent for SEM observation and rim part has constant width of about 20 nm. This structure is particularly interesting, because it can be carbon thin film supported by carbon micro-ring.

Keywords: mica; intercalation; template carbons

INTRODUCTION

Mica being a kind of layer silicate has tetrahedral and octahedral crystalline network with two-dimensional spread. A fluorine expandable mica (EM) was specially synthesized using the original method developed at AIST Kyushu. Because of wider crystalline size along the layer direction than other kind of layer silicates, EM can provide two-dimensional expanse between its lamellae for various kinds of guest substances.

The intercalation and carbonization of organic compounds in layered clay minerals have already been discussed by some workers [1,2]. In particular, Kyotani and Tomita have reported preparation of highly oriented graphite from polyacrylonitrile in the interlamellar opening of montmorillonite, followed by establishment of "template carbonization" using various host materials and precursors [2–5]. The present paper describes a unique structure in carbon prepared between the lamellae of EM using organic liquids, such as pyridine and quinoline, for carbon source.

EXPERIMENTAL

Figure 1 illustrates the chemical structure of EM. The structural formula calculated from the chemical compositions based on $O_{10}F_2$ is described as $Na_{0.6-0.7}Mg_{2.8-2.85}Si_4O_{10}F_2$. The intercalation of organic compound (mainly quinoline) into the lamellae of EM was easily achieved by mixing them with stirring and standing overnight at room temperature. After filtration for removing supernatant liquid, intercalated EM, being swelled owing to a large amount of liquid between layers, was heat-treated in an electric furnace under inert atmosphere at the temperatures between 250–750°C for 3 hr. The heating rate was 20°C/min. The silicate matrix was dissolved in concentrated hydrofluoric acid, and residual fluorides were removed by hydrochloric acid, followed by thoroughly washing with distilled water.

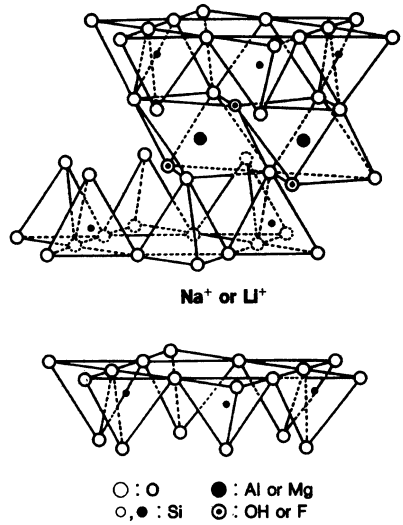

FIGURE 1 Chemical structure of fluorine expandable mica.

An X-ray powder diffraction (XRD) pattern of each sample was collected using a powder diffractometer equipped with a copper target X-ray tube. The images of obtained samples were taken with FE-SEM operating at 5 kV of accelerated voltage and TEM at 200 kV.

RESULTS AND DISCUSSION

Powder X-ray diffraction profiles of as-prepared and heat-treated EM are shown in Figure 2. The interlamellar spacing of as-prepared EM was 1.2 nm. The spacing was maintained up to 250°C and then decreased to 0.94 nm during heat treatment. The reason for this decrement should be sought in escape of water from the lamellae. The crystalline structure of EM is no longer stable beyond 800°C of heat treatment temperature (HTT). Figure 3 shows the XRD profiles of quinoline-intercalated EM during heat treatment up to 750°C. In Figure 3(a) a new peak appeared around 1.5 nm and it was attributable to the expanded interlamellar spacing due to insertion of quinoline molecules. Being taken into account of the increase of interlamellar spacing and thickness of the molecule, monolayer-like quinoline may stretch between the lamellae. As shown in Figure 3(b) and (c), the quinoline-derived carbonaceous compound remained in the mica layer although HTT is much higher than the boiling point of quinoline. During the heat treatment, the color of quinoline/EM composite turned black from

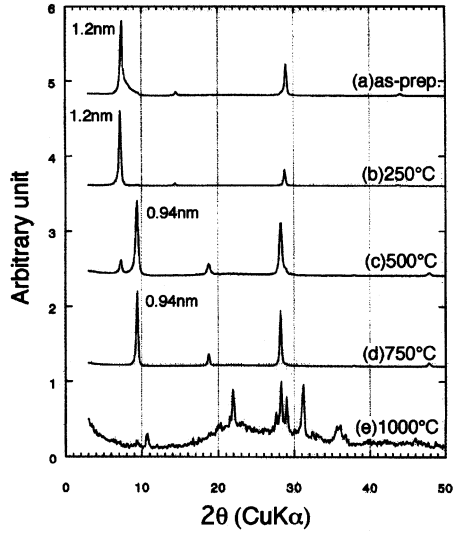

FIGURE 2 X-ray diffraction profiles of as-prepared and heat-treated EM.

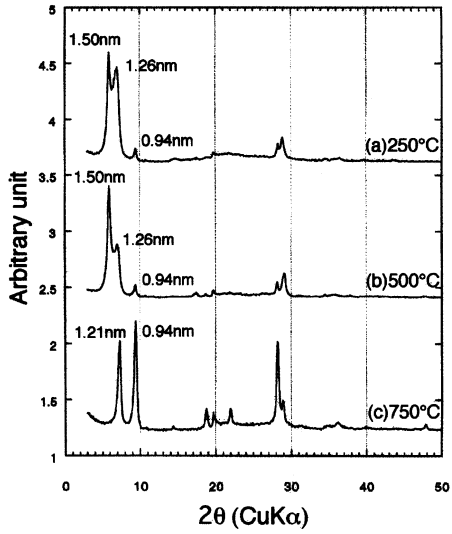

FIGURE 3 X-ray diffraction profiles of heat-treated quinoline/EM composite.

white, therefore, the sample was found to contain certain amount of carbon (or carbonaceous compound) derived from the quinoline. This means the enclosed molecules, even in the case of small molecular weight, in the restricted space of EM can polymerize by heat treatment. In addition, specific surface areas estimated by nitrogen adsorption at 77 K were 3.3 m^2/g for as-prepared EM and 3.5 m^2/g for carbon/EM composite heat-treated at 750°C. After elimination of mica network by acid solutions, as shown in Figure 4, obtained carbon maintained original particle shape of EM (inset photograph). However, the stacking of carbon particles is evidently transparent; the electron beam accelerated by only 5 kV can reach underlying layer of the stacking. This is because the thickness of each carbon particle spread two-dimensionally is suggested to be very thin. In addition, if subtract the edge effect which often occurs with SEM observation, an unusual emphasizing of verge along the particles can be seen in Figure 4. The result of nitrogen adsorption at 77 K gave a type-II isotherm (IUPAC) and 147 m^2/g of specific surface area. A shape of the isotherm indicates a nonporous characteristic, viz. the BET surface area can be approximately equal to the geometrical surface area of particles. On the other hand, the use of pyridine, whose boiling point is by far lower than that of quinoline, for an intercalate gave similar result.

Following TEM observation revealed unique structure of the sample as shown in Figure 5. Namely, the obtained carbon appears to consist a very thin film surrounded by a belt-like edge. The thickness of film part is poorly

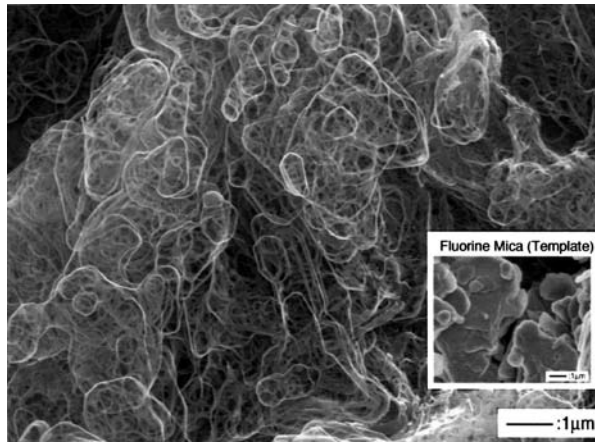

FIGURE 4 Scanning electron micrographs of quinoline-derived carbon separated from EM matrix (inset photograph is original EM particles).

estimated. The rim part, being closed circle, has constant width of about 20 nm. From micrograph images, the places in which two structural parts formed are obviously the edge of EM particles (for rim part) and the interlamellar space in them (for film part).

High-resolution TEM observations permitted the identifying of microstructure in the two parts. Figure 6 demonstrates the lattice fringe image and the electron diffraction patterns at the peripheral area of a particle. In addition to these, an inferred structural model is also presented. Parallel orientation of 002 lattice along the longitudinal direction can be clearly seen in the rim part and no apparent orientation in the film part. The electron diffraction pattern from each part is consistent with the blight field observation; 002 arc from the rim and 10 and 11 rings, indicating perpendicular stacking of carbon hexagonal layers to the electron beam, from the

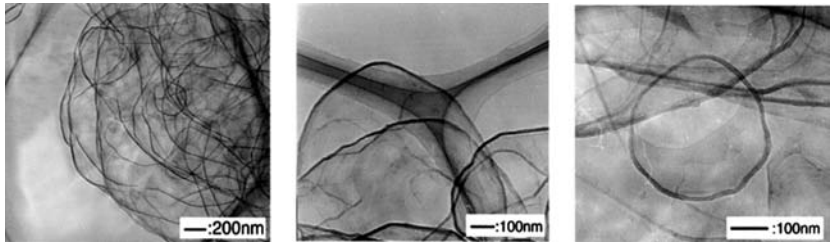

FIGURE 5 Transmission electron micrographs of quinoline-derived carbon separated from EM matrix.

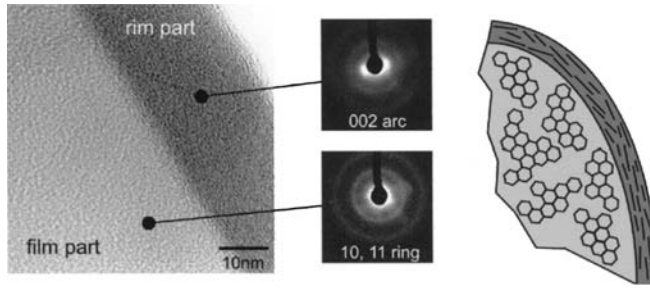

FIGURE 6 Lattice fringe image and electron diffraction patterns of peripheral area of the carbon particle. Right-hand illustration is a model inferred from micrographic information.

film. Considering above micrographic information, the schematic representation of the structure can be drawn in the manner presented in Figure 6. If this model is appropriate, the direction of carbon layers is almost orthogonal to one another.

Consequently, it should be clarified the connecting manner of two carbon layers in the border. However, any evidence for determining the link between them, regardless of whether they are connected or not, has not been found.

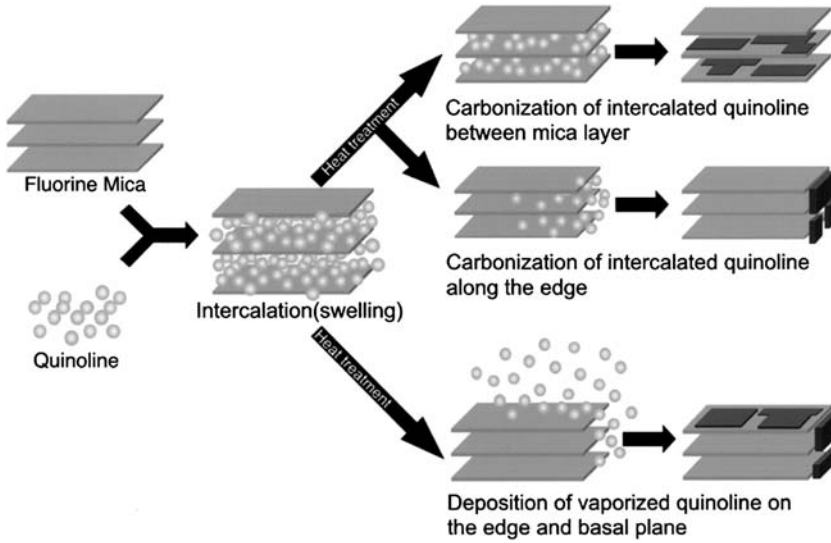

FIGURE 7 Feasible pathways for quinoline-derived carbon.

Figure 7 exhibits the feasible pathways for reaching the quinoline-derived carbon structure. As described above, the film and rim part were evidently formed in the interlayer space and at the edge of EM crystal, respectively. The formation mechanism of the film part is reasonable to explain. Despite the volatile compound, a part of intercalated quinoline remained and was able to carbonize in the narrow space between the silicate walls. However, the amount of remnant quinoline was not enough to make a carbon layer spread over the interlamellar space, because the XRD measurement shows that only monolayer of quinoline remained in a space after heat treatment at 250°C (near the boiling point of quinoline). Hence, island-like graphene sheets formed by template carbonization in each space probably stacked when silicate matrix was removed. For the rim part, some portion of quinoline, mainly placed on the peripheral of a particle, may move to the edge and deposited there. However, compared with the film part, much larger amount of carbon have deposited on the edge of EM. Thus the formation of rim part cannot be quantitatively explained only by intercalated quinoline, which hardly supplies the adequate amount of carbon source. Accordingly, the different pathway should be required. For this reason, chemical vapor deposition (CVD) on the edge from gaseous phase should be considered. The quinoline-intercalated EM was swelled on account of a large amount of liquid between layers. Under the elevated temperature, certain amount of intercalated quinoline surely vaporized-remnant molecules will mainly form the film part- and filled up the furnace tube. This caused carbon deposits on the edge and exposed basal planes of EM at higher temperature. This CVD process can be regarded as the predominant rout for forming the rim part.

CONCLUSIONS

Novel carbon structure was obtained by carbonization of organic liquids using fluorine expandable mica as a template. The structure proved to be very thin film surrounded by the rim having constant width of ca. 20 nm. The formation of the structure was considered to be due to the combination of carbonization between layers and CVD onto outer surface of EM.

This structure is particularly interesting, because, in other words, it may possibly be carbon thin film supported by carbon ring. As far as we were aware, this morphology of carbon has not been reported. From now on, more characteristic investigation, especially change in the structure during carbonization and graphitization, should be needed. Besides, physical properties should also be explored to apply this material for adsorbents, batteries, capacitors and so on.

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