Formation of Oriented Carbon Nanofibrils in Pyrolyzed Product of Terephthalic Acid Disodium Salt†

Katsumi Kamegawa†
National Institute of Advanced Industrial Science and Technology (AIST) Kyushu, Shuku, Tosu, Saga 841-0052, Japan,

Masaya Kodama
AIST Tsukuba, Onogawa, Tsukuba, Ibaraki 305-8569, Japan,

Keiko Nishikubo, Hiroshi Yamada, and Yoshio Adachi
National Institute of Advanced Industrial Science and Technology (AIST) Kyushu, Shuku, Tosu, Saga 841-0052, Japan

Hisayoshi Yoshida
Department of Environmental Symbiosis Engineering, Kurume Institute of Technology, Kamitsu 2228-66, Kurume, Fukuoka 830-0052, Japan
(Received 12 October 2005; Accepted 1 December 2005; Published 20 December 2005)

Terephthalic acid disodium salt (TADS), C_8H_4(COO Na)_2, pyrolyzes in a solid phase at above 600°C. That pyrolysis produces a composite of carbon nanofibrils and fine sodium carbonate crystals. The carbon nanofibrils are amorphous and have 10-200 nm diameter. Forms of the carbon nanofibrils depend on experimental conditions. The carbon fibrils formed at 600°C are slightly entangled and bunched into bundles. Moreover, those bundles are aligned roughly in the direction parallel to the b-axis of the pristine TADS crystals. Wide-angle x-ray diffraction images of a pyrolytic product from a TADS crystal showed those arcs attributable to monoclinic sodium carbonate, indicating the rough alignment of the sodium carbonate crystals. Carbon nanofibrils are inferred to form as a result of exclusion by roughly aligned sodium carbonate crystals. [DOI: 10.1380/ejssnt.2005.484]

Keywords: X-ray diffraction; Self-assembly; Carbon; Nano-fibrils; Porous solids

I. INTRODUCTION

It is generally believed that solid phase carbonization of crystalline carbon precursors forms disordered carbon materials because the elimination of noncarbon elements as gases involves a distortion of the carbon structure. In spite of such difficulties, some attempts have been devoted to the fabrication of carbon materials with regular structure from the atomic to mesoscopic levels. Gogotsi, et al. fabricated diamond nanocrystals through a reaction between crystalline silicon carbide and chlorine-containing gas at 1000°C [1, 2]. Similar reactions of metal carbides with chlorine gas were also investigated by Zheng, et al. and by Leis, et al., who respectively reported formation of onion-like carbon [3] and barrel-like multi-wall nanoparticles [4]. Furthermore, Kusunoki, et al. found that YAG-laser-assisted heating of β-silicon carbide at 1700°C produces an epitaxial carbon nanotube film on the carbide surface [5–7]. We have examined the thermal decomposition of numerous crystalline organic compounds and found that pyrolysis of the crystals of terephthalic acid disodium salt at above 600°C forms a composite of roughly aligned carbon nanofibrils and fine sodium carbonate crystals. Herein, we report a simple process for production of oriented carbon nanofibrils and their microstructures that were elucidated by XRD, SEM, and TEM.

II. EXPERIMENTAL

Terephthalic acid disodium salt (TADS), C_8H_4(COO Na)_2, was prepared as follows: terephthalic acid (0.25 mol) was neutralized by dissolving into a sodium hydroxide solution (0.5 mol/dm³, 1 dm³). The resultant salt solution was treated with No. 5C filter paper to remove unreacted terephthalic acid and impurities. The filtrate was allowed to dry at room temperature.

The TADS crystals were placed in an alumina boat and heated at 550-900°C for 1 h in an argon flow (100 cm³/min). The heating rate was 200°C/h. The gases evolved during the pyrolysis of TADS were followed by mass spectrometry. The product was washed successively with water, 1 N HCl, and water again to remove unreacted salt and the sodium compounds formed by pyrolysis. The carbonaceous products were dried at 120°C. The products are called, for example, TADS600 and TADS600C: the former is a pyrolyzed product at 600°C, whereas the latter is the carbonaceous product obtained from TADS600 by washing and drying.

Wide-angle x-ray diffraction images were recorded using a four-circle X-ray diffractometer (Rigaku Co.) with an imaging plate. The monochromatized CuKα X-ray was passed through a pin hole (1 mm), and was transmitted through a TADS625 sample from the three axes of the pristine TADS crystal. A diffraction image was recorded on an imaging plate. The camera radius was 56 mm and the exposure time was 5 min.
FIG. 1: TGA curve for TADS and gases evolved during pyrolysis.

FIG. 2: Yields of pyrolyzed and carbonaceous products.

III. RESULTS AND DISCUSSION

Figure 1 shows a TGA curve for TADS and the gases evolved during pyrolysis of TADS. Pyrolysis of TADS involves three stages at temperatures of ca. 550-650°C, 650-750°C, and 750-950°C. Principal constituents of the evolved gases were hydrogen, carbon monoxide, and carbon dioxide at the first stage, hydrogen and carbon monoxide at the second stage, and carbon monoxide at the third stage. As explained later, the first stage corresponds to conversion of TADS crystals into a composite of a carbonaceous material and sodium carbonate, the second stage to polycondensation of the carbonaceous material, and the third stage to the reaction between carbon and sodium carbonate.

The yields of the pyrolyzed and carbonaceous products on a starting material basis are shown in Fig. 2. The yield of the pyrolyzed products shows two large decreases at ca. 600°C and 850°C. On the other hand, the yield of carbonaceous products increased markedly above 550°C, reached a maximum value of 34% at 600°C, and declined gradually thereafter. The XRD profiles for the pristine TADS, pyrolyzed products, and carbonaceous products are shown in Fig. 3. The profile for TADS was consistent with that of orthorhombic TADS (a = 3.548, b = 10.816, and c = 18.994) [8]. The profile was completely changed when TADS was heated above 600°C, and the profiles for the pyrolyzed products show that they consist of amorphous carbon and monoclinic sodium carbonate crystals. The intensity of the diffraction peaks of the carbon for TADS600 and TADS600C was very weak and broad, indicating that the carbonaceous products are amorphous. As the temperature was elevated up to 900°C, the intensity for the carbon increased, but that for the sodium carbonate decreased. Regarding pyrolysis at higher temperatures, the formation of a metallic and highly reactive product was observed near the outlet of the reaction tube. The authors inferred that sodium metal was formed in the reaction between carbon and sodium carbonate at those higher temperatures [9, 10].

SEM and TEM images of TADS crystals, TADS600C, and TADS625C are shown in Fig. 4. The crystal form of TADS is plates (Fig. 4a). XRD analysis of a single crystal of TADS revealed that the TADS crystal is orthorhombic and that the axes are aligned as shown in Fig. 4a. The TADS shape was almost maintained in TADS600C (Fig. 4b). The TADS axes are also used for TADS600C and TADS625C to express the directions and planes of the carbon plates. A quite unique fibrous carbon structure appeared (Fig. 4d) when the skin structure of the ab plane of TADS600C was fractured (Fig. 4c). The diameter of the carbon nanofibrils was 10-200 nm. The carbon fibrils were slightly entangled and bunched into bundles. Moreover, the bundles were roughly aligned in the direction parallel to the b-axis. Another type of carbon nanofibril was found in TADS625C (Figs. 4e-4h). The carbon
The nanofibril diameter was similar to that for TADS600C. Most of the carbon nanofibrils were also parallel to the $b$-axis, but short carbon nanofibrils were aligned in the direction perpendicular to the $b$-axis. These unique carbon nanofibrils have not been described in published reports.

The average carbon structure of the nanofibrils was amorphous (Fig. 3), and the carbon structure, even at the surface region, was also amorphous (Fig. 4h). The lack of regularity in the carbon structure suggests that the sodium carbonate crystals play an important role in the formation of the aligned carbon nanofibrils. Wide-angle x-ray diffraction images of a piece of TADS625 prepared from a TADS crystal were recorded from directions of the three axes of the pristine TADS crystal using an imaging plate to obtain further insight. The three images in Fig. 5 were mutually different; some arcs existed along with broad lines. All arcs and lines were attributed to monoclinic sodium carbonate. These results prove the rough orientation of sodium carbonate crystals, although great uncertainty remains regarding the mechanism of the oriented growth of the sodium carbonate crystals. The above findings imply the following mechanism of the growth of aligned amorphous carbon nanofibrils. Amorphous carbon and sodium carbonate are formed on the pyrolysis of TADS crystals. At that time, the sodium carbonate crystals grow preferentially in a roughly oriented fashion. The amorphous carbon is excluded by the oriented sodium carbonate crystals, and carbon nanofibrils are located between the fine sodium carbonate crystals. Consequently, the amorphous carbon nanofibrils are roughly aligned to the axis of the TADS crystals.
FIG. 5: X-ray transition photographs of TADS625 taken from directions parallel to (a) a-, (b) b-, and (c) c-axes.

[1] Y. Gogotsi, S. Weiz, D. A. Ersoy, M. J. McNallan, Nature 411, 283 (2001).
[2] S. Weiz, Y. Gogotsi, M. J. McNallan, J. Appl. Phys. 93, 4207 (2003).
[3] J. Zheng, T. C. Ekstrom, S. K. Gordeev, M. Jacob, J. Mater. Chem. 10, 1039 (2000).
[4] J. Leis, A. Perkson, M. Arulepp, M. Kaarik, G Svensson, Carbon 39, 2043 (2001).
[5] M. Kusunoki, M. Rokkaku, T. Suzuki, Appl. Phys. Lett. 71, 2620 (1997).
[6] M. Kusunoki, J. Shibata, M. Rokkaku, T. Hirayama, Jpn. J. Appl. Phys. 37, L605 (1998).
[7] M. Kusunoki, T. Suzuki, K. Kaneko, M. Ito, Phil. Mag. Lett. 79, 153 (1999).
[8] J. A. Kaduk, Acta Cryst. B56, 474 (2000).
[9] D. W. McKee, D Chatterji, Carbon 13, 381 (1975).
[10] D.W. McKee, Fuel 62, 170 (1983).