

SYNTHESIS OF A NEW GRAPHITE-LIKE MATERIAL OF COMPOSITION $BC_6N_2(H)$ AND THE STRUCTURE OF ITS PRECURSOR

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Introduction

The structural similarity and the quite different physical property between graphite and hexagonal boron nitride (h-BN) have motivated the synthesis of new boron/carbon/nitrogen materials (B/C/N materials) based on the graphite network. It is expected that B/C/N materials interact with acids or bases moderately and is a semiconductor [1], because their properties may be intermediate between those of graphite and h-BN.

The stoichiometric compounds BC_2N [2,3], BC_3 [2], C_3N [2] and BC_4N [3] were synthesized by CVD or solid-phase pyrolysis of precursors. We have recently synthesized a graphite-like layered material of composition BC_3N by the interaction of poly(acrylonitrile) or acrylonitrile monomer with boron trichloride and found that it forms Li-intercalated compound and behaves as a semiconductor [4]. During the CVD reaction of acrylonitrile with boron trichloride, an adduct of white powders formed at cool zone in the CVD reaction tube [4].

In this paper, we report the syntheses and structures of an adduct $(CH_2CHCN)_2:BCl_3$ and a new graphite-like material of composition $BC_6N_2(H)$. Electrical conductivity and Li-intercalation for $BC_6N_2(H)$ are also reported.

Experimental

Preparation and Pyrolysis of adduct: BCl_3 vapor (5.0×10^{-5} m³/min) and N_2 (5.0×10^{-5} m³/min) were introduced into the flask which contained acrylonitrile liquid (50 g) at room temperature. The liquid-gas reaction was carried out for 3.5 h. The solid of adduct obtained was then set in a quartz tube and heated at a temperature between 500 and 1000 °C by electric furnace under N_2 atmosphere for 1 h.

Preparation of $BC_xN_y(H)$ film: A quartz glass plate ($30 \times 5 \times 1$ mm) as a substrate was set at the center of a quartz reaction tube. Acrylonitrile vapor (2.0×10^{-5} m³/min) carried by N_2 (1.4×10^{-4} m³/min) and BCl_3 gas (1.0×10^{-5} m³/min) were introduced to the hot zone (1000 °C) of the reactor.

Electrical conductivity was measured for the $BC_xN_y(H)$ film deposited on the quartz substrate by using a d.c. four-probe technique at 20~700 °C under N_2 atmosphere.

Li intercalation: 0.56 g of the powders obtained by CVD was added into a 4.0×10^2 mol/m³ $Li^+C_{10}H_8$ /Tetra-

hydrofuran (THF) solution (1.0×10^{-4} m³) and then the mixed solution was stirred for 1 week. The product was filtrated and washed with THF in a dry box.

Results and Discussion

When the BCl_3 gas was introduced into the flask, an exothermic reaction occurred and fine white powders formed in the gas phase as well as on the CH_2CHCN liquid. The white powders could be dissolved in the liquid at the first time and deposited on the liquid in the flask as the reaction proceeded. The color of powders and liquid gradually changed to yellow, when the $CH_2CHCN : BCl_3$ molar ratio was about 10 : 1. All the CH_2CHCN liquid changed to yellow~orange soft solid when the $CH_2CHCN : BCl_3$ molar ratio was 2 : 1.

Sharp X-ray diffraction pattern for the adduct $(CH_2CHCN)_2:BCl_3$ has a integer relationship suggestive of cubic or quasi-cubic symmetry: $d^2(\text{nm})^{-2}$ (I/I_0); 1.67(w), 6.68(vs), 13.3(vw), 15.0(vw), 41.6(vw).

The 2 : 1 adduct became brownish hard solid after a storage under N_2 at room temperature for 1 month. Even the yellowish solution ($CH_2CHCN : BCl_3 = 10 : 1$) became brownish soft solid after 1 month. The UV-Visible spectra (Fig.1) for the solution ($CH_2CHCN : BCl_3 = 10 : 1$) changed smoothly over a one month period with strong absorbance shifting from a 400 nm in fresh solution to 800 nm in aged solutions. These results suggest that the conjugated double bonds in the 2 : 1 adduct and the 10 : 1 solution increased with time. In other words, CH_2CHCN gradually polymerized at room temperature by the interaction with BCl_3 .

In this reaction, each BCl_3 molecule can act as a Lewis acid for one Lewis base of a nitrogen of -CN group in the CH_2CHCN . The composition $(CH_2CHCN)_2:BCl_3$ can be interpreted by the interaction of each BCl_3 molecule with half of the available nitrogen in the dimerized $(CH_2CHCN)_2$. This result is also supported by ¹³C-NMR study.

Black powders were obtained by the pyrolysis of the adduct $(CH_2CHCN)_2:BCl_3$ at 500~1000 °C. HCl gas was eliminated during the pyrolytic reaction. The elemental analyses indicated the black powder obtained by the pyrolysis at 1000 °C had a composition $BC_{5.8-6.2}N_{1.8-2.0}H_{2-4}$ which is described as $BC_6N_2(H)$ in this paper.

Broad X-ray powder diffraction and sharp electron

diffraction pattern indicate that $BC_6N_2(H)$ is composed of very small single crystals which has the graphite-like layered structure.

Figure 2 indicates a possible atomic arrangement in the layer of BC_6N_2 , which is derived from the interpretation of ESCA spectra and the following assumptions deduced by its reaction: (a) The original monomer chain C-C-C-N of acrylonitrile can remain in the BC_6N_2 network, (b) A B-N bond can be made from the coordinate bond of B-N caused by the formation of the adduct $(CH_2CHCN)_2:BCl_3$, (c) B-B and N-N bonds cannot be easily made, because of the thermodynamically implausible reaction of B-Cl and B-Cl $\{\Delta G = 340 \text{ kJ/mol}$ for the reaction $BCl_3 \rightarrow B + 1.5Cl_2$ at $1000^\circ C\}$ and a repulsion of lone-pair electrons between nitrogen atoms, respectively. The structure can be generated by repetition of an unit structure NCCCCCNB, which could reflect the main framework of the adduct $(CH_2CHCN)_2:BCl_3$ as the precursor.

Black shiny film was obtained on the quartz substrate by CVD method. It had a composition $BC_{5.8-6.0}N_{1.4-1.5}H_{0.1-0.2}$ whose nitrogen and hydrogen contents were smaller than that of $BC_6N_2(H)$ obtained by the pyrolysis of adduct, probably because the nitrogen was eliminated in stable forms such as NH_3 or N_2 in the gas phase during the CVD reaction.

$BC_6N_{1.5}(H)$ film shows the basal-plane conductivity $531 \Omega^{-1}cm^{-1}$ at room temperature which is larger than that of $BC_3N(H)$ plate prepared by CVD ($88.5 \Omega^{-1}cm^{-1}$, gas molar ratio; $CH_2CHCN : BCl_3 = 1 : 1$) [4]. Activation energy calculated from the Arrhenius plot is $2.72 \times 10^{-2} eV$.

The reduction with $Li^+C_{10}H_8^-/THF$ solution for $BC_6N_{1.5}(H)$ yielded a Li intercalated compound. Almost no change in color was detected. The X-ray diffraction analysis indicated that the compound had a d-spacing of 0.87 nm in the direction of c-axis. This compound may be assigned as a 1st stage with THF as well as Li in the interlayer spacing, which was reported for graphite in the similar case.

Conclusions

A new graphite-like layered material of composition $BC_6N_2(H)$ is synthesized by the pyrolysis of $(CH_2CHCN)_2:BCl_3$ adduct, which is prepared by the interaction of acrylonitrile with boron trichloride at room temperature. $BC_6N_{1.5}(H)$ film prepared by CVD reaction ($CH_2CHCN:BCl_3 = 2:1$) has a conductivity of $531 \Omega^{-1}cm^{-1}$ at room temperature and behaves as a semiconductor. The reduction of $BC_6N_{1.5}(H)$ with $Li^+C_{10}H_8^-/THF$ solution has yielded a lithium intercalated compound with a repeat distance of 0.87 nm.

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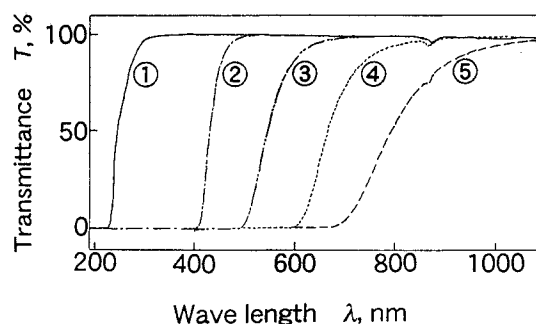


Figure 1. Change in UV-Visible spectrum of $CH_2CHCN : BCl_3 = 10 : 1$ solution. ① CH_2CHCN ② $CH_2CHCN + BCl_3$ (just after preparation) ③ 2 days later ④ 6 days later ⑤ 1 month later

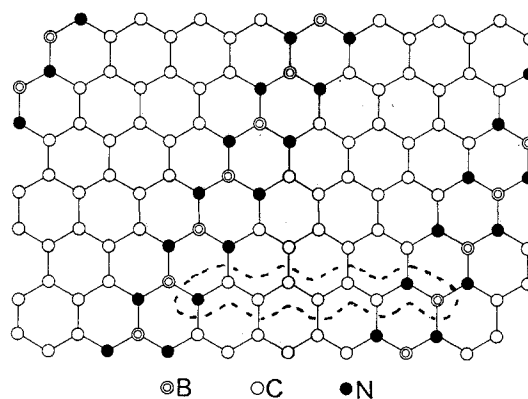


Figure 2. Possible atomic arrangement of BC_6N_2 synthesized by the pyrolysis of the adduct $(CH_2CHCN)_2:BCl_3$. An unit structure NCCCCCNB is surrounded by dotted line.