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Solid State Communications 139 (2006) 501–505

solid state communications

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Nitrogen-rich carbon nitride materials shock-synthesized from carbon tetrahalide and sodium dicyanoamide

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Received 21 April 2005; received in revised form 20 July 2006; accepted 20 July 2006 by A. Pinczuk
Available online 4 August 2006

Abstract

Shock reactions between CX_4 (X = Br or I) and $NaN(CN)_2$ were investigated to prepare carbon nitrides. The post shock samples were characterized by the powder X-ray diffraction (XRD) technique. The XRD spectrum of the product showed a peak in the range of 0.324–0.336 nm in d-value corresponding to the (002) basal plane diffraction in graphitic structure. Elemental analysis (C, H, N, O) of the product showed that the atomic ratio of nitrogen to carbon (N/C) ranged from 0.38 to 1.3. Analysis of data revealed that the d-value increased and the nitrogen content decreased with the increase of the impact velocity.

PACS: 62.50.+p; 81.05.Tp; 81.40.Vw

Keywords: A. Nanostructures; B. Shock compression; E. Strain, High pressure; E. X-ray and X-ray spectroscopies

Prediction of novel phases of C_3N_4 with high bulk moduli [1,2] has produced vast number of studies [3–5] on carbon nitride materials. From the conception analogous to the high-pressure synthesis of diamond from graphite, graphitic C_3N_4 (g-C_3N_4) is considered to be an appropriate precursor for preparing the predicted phase. Proximity to the stoichiometry of C_3N_4 in graphitic carbon nitride materials has been attempted in several ways [6–11], including shock compression techniques [12–15]. The starting materials generally employed have clustered on 1,3,5-triazine-based compounds. The method of preparation includes polycondensation of melamine [6–9,15], condensation of melamine and cyanuric chloride [8], pyrolysis of trichloromelamine [10], and reaction of cyanuric chloride with sodium amide [11]. In this study we adopted precursors such as carbon tetrahalide (CX_4 ($X = \mathrm{Br}, \mathrm{I}$)) and sodium dicyanoamide ($NaN(CN)_2$) [13] which were exposed to shock compression as described in Eq. (1). The starting materials provide adequate composition of carbon and nitrogen for synthesis of C_3N_4 materials. Shock compression generates dynamic high-pressure and high-temperature to achieve denser states. Chemical reaction induced by shock wave has a characteristic feature of adiabatic compression attended with increase of entropy. Pulsed pressure of short duration (typically ~1 μs) where abrupt increase and release of pressure are realized may provide an appropriate condition for approaching the metastable phase. We now report a new synthetic route to graphitic nitrogen-rich carbon nitride materials.

$$\chi CX_4 + 4\chi \mathrm{NaN(CN)_2} \rightarrow [\mathrm{C_3N_4}]_{3\chi} + 4\chi \mathrm{Na}X. \qquad (1)$$

All manipulations for the loading of starting materials into sample containers were performed under dry N_2 atmosphere. In a typical experiment, CX_4 (X = Br, I) and $NaN(CN)_2$ were mixed in an agate mortar with a molar ratio of 1:4 and ground with an agate pestle for 5 min. The sample was then placed in a sample container (Cu) and pressed at 300 $\mathrm{kg/cm^2}$ for 5 min. The evaluated densities ($\mathrm{g/cm^3}$) for the samples (1.8–2.2 ($X = \mathrm{Br}$), 2.5 ($X = \mathrm{I}$)) were consistent with the calculated ones for the 1:4 mixture of CX_4 and $NaN(CN)_2$ (2.05 ($X = \mathrm{Br}$), 2.26 ($X = \mathrm{I}$)). After the screw lid (Cu) was equipped, the dip around the lid was covered with Araldite® to protect the sample from air and moisture. The container was held in the target assembly and used as the target of a propellant gun for shock-recovery experiments [16]. Projectiles with flyer plates (Cu) of 2 mm thickness were accelerated in a

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doi:10.1016/j.ssc.2006.07.021

Table 1
Shock-recovery experiments for preparation of carbon nitride materials

Shot#	Reactants	Impact velocity v_{imp} (km/s)	Shock pressure P (GPa)	Products	XRD d (nm)	Elemental analysis (wt%)					Atomic N/C
						C	H	N	O	Total	
1173	$NaN(CN)_2$ (518 mg), CBr_4 (480 mg)	0.652	13	Dark grey powder (13 mg[a])	0.324	–	–	–	–	–	–
1169	$NaN(CN)_2$ (518 mg), CBr_4 (480 mg)	0.686	14	Dark brown powder (25 mg)	0.324	34.1	1.89	49.2	11	96.19	1.24
1177	$NaN(CN)_2$ (264 mg), CBr_4 (240 mg)	0.890	18	Brown powder (51 mg)	0.325	30.8	<0.01	45.3	11	87.1	1.26
1178	$NaN(CN)_2$ (264 mg), CBr_4 (240 mg)	1.02	21	Dark brown powder (67 mg)	0.327	35.8	2.09	46.1	9.4	93.39	1.10
1174	$NaN(CN)_2$ (246 mg), CBr_4 (224 mg)	1.09	23	Brown powder (75 mg)	0.326	–	–	–	–	–	–
1166	$NaN(CN)_2$ (518 mg), CBr_4 (480 mg)	1.09	23	Black powder (24 mg)	0.327	–	–	–	–	–	–
1179	$NaN(CN)_2$ (264 mg), CBr_4 (240 mg)	1.11	24	Black powder (64 mg)	0.326	–	–	–	–	–	–
1180	$NaN(CN)_2$ (264 mg), CBr_4 (240 mg)	1.20	26	Black powder (64 mg)	0.326	39.4	2.11	43.9	10	95.41	0.955
1164	$NaN(CN)_2$ (532 mg), CBr_4 (480 mg)	1.24	27	Black powder (228 mg[a])	0.32–0.33[b]	–	–	–	–	–	–
1165	$NaN(CN)_2$ (532 mg), CBr_4 (480 mg)	1.33	29	Black powder (259 mg[c])	0.329[d]	–	–	–	–	–	–
1168	$NaN(CN)_2$ (518 mg), CBr_4 (480 mg)	1.43	<32	–[e]	–	–	–	–	–	–	–
1170	$NaN(CN)_2$ (242 mg), CBr_4 (220 mg)	1.46	33	Black powder (44 mg)	0.327	48.4	<0.01	38.4	8.5	95.300	0.680
1175	$NaN(CN)_2$ (249 mg), CBr_4 (226 mg)	1.50	34	Black powder (44 mg)	0.336	58.6	<0.01	29.2	8.2	96	0.427
1167	$NaN(CN)_2$ (518 mg), CBr_4 (480 mg)	1.64	<38	–[e]	–	–	–	–	–	–	–
1172	Cu powder (1.962 g), product of #1164 (0.218 g)	1.51	34	Black powder (59 mg)	0.330	47.7	<0.01	33.5	13	94.2	0.602
1176	Cu powder (1.800 g), product of #1165 (0.200 g)	1.90	45	Black powder (64 mg)	0.335	55.9	<0.01	24.9	12	92.8	0.382
1196	$NaN(CN)_2$ (264 mg), CI_4 (376 mg)	1.01	21	Black powder (127 mg)	0.328	–	–	–	–	–	–

[a] The product was not treated with HNO_3aq.
[b] Exact value was not acquired due to partial overlap of another peak.
[c] The amount before treatment with HNO_3aq is described. 200 mg of the product was used in #1176.
[d] 59 mg of the product was treated with HNO_3aq to give a black solid (2 mg) which was subjected to the XRD measurement.
[e] Products were not obtained due to breakage of sample containers.

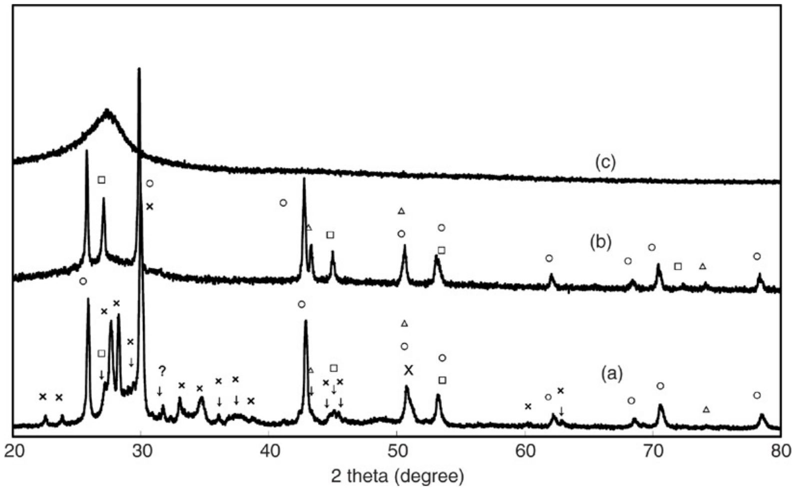

Fig. 1. XRD patterns of sample obtained in shot 1169. As recovered (a), after washed by water (b), and after treatment with HNO_3 (c), ○ = NaBr, × = NaC_2N_3, □ = CuBr, Δ = Cu, ? = unknown.

launcher and impacted onto the target. The impact velocity was measured with a magnetoflyer method [17]. Due to lack of Hugoniot data for the starting mixture, impact velocity (v_{imp}) has been used as a measure for harshness of shock condition. The peak shock pressure (P) (described in Table 1) was calculated with the shock impedance-matching method [18, 19] assuming that the pressure was equilibrated with container. The shock temperature is not estimable because Hugoniot and thermodynamic data are unavailable. After shock treatment the recovered sample containers were opened to give solid materials.

Powder X-ray diffraction (XRD) spectra of the products were recorded on Rigaku RINT 2200V/PC with Cu Kα radiation generated at 40 kV and 50 mA. In the XRD spectrum (5–110°) of the product (X = Br, #1169) as in part depicted in Fig. 1(a), the strongest set of 14 peaks was attributed to

NaBr. This fact clearly shows that the reaction proceeded. The second strongest set of 18 peaks belongs to α-NaN(CN)$_2$ [20]. Identification of another peak was disturbed by these intense peaks. CBr$_4$, β-NaN(CN)$_2$, and the trimer of NaN(CN)$_2$ were significantly not recognizable. To remove the obstacles disturbing identification of peaks with low intensity, the product of #1169 was washed with water (rt) as a test. In the XRD spectrum (5–110°) of the resultant product (partly shown in Fig. 1(b)), the strongest set of peaks was attributable to NaBr. The second strongest set of 4 peaks belongs to γ-CuBr. This fact implies formation of Br$_2$ which subsequently reacted with the container (Cu). The third strongest set of 5 peaks results from Cu. The tiny peaks of γ-CuBr and Cu are now recognizable also in Fig. 1(a). The product was further washed with HNO$_3$aq (13 N) to eliminate these coppery materials. The XRD spectrum (5–110°) of the final product (partly shown in Fig. 1(c)) showed a broad peak.

Typically the product (X = Br) after opening the sample container was suspended in HNO$_3$aq (13 N, 50 mL). The precipitates were washed with distilled water (rt and then 60 °C), dried at 120 °C with silica gel, and subjected to XRD measurements and elemental analyses. The results are summarized in Table 1 (the first 14 entries). In all cases except #1168 and #1167, products were obtained as stable powder. The typical XRD patterns of the products are shown in Fig. 2((a), (b), and (c)). In the XRD spectra of the products, the strongest peak at 26.5–27.5° (0.324–0.336 nm) corresponds to the (002) basal plane diffraction in the graphitic structure. These data are compatible with the calculated (d = 0.336 nm [3]) and experimental values of interlayer spacing for g-C$_3$N$_4$ and related compounds (d = 0.327 [7], 0.322 nm [11] for proposed g-C$_3$N$_4$, d = 0.325 nm for quasi graphitic carbon nitride [9], d = 0.324 nm for C$_3$N$_{4+x}$ [10], d = 0.329 nm for [(C$_3$N$_3$)$_2$(NH)$_3$]$_n$ [21], d = 0.322 nm for C$_6$N$_9$H$_4^+$Cl$^-$ [22], d = 0.327 nm for C$_6$N$_7$(NH$_2$)$_3$ [23], d = 0.323 nm for [(C$_3$N$_3$)$_2$(NH)$_3$]$_n$ [24]).

As shown in Fig. 3, the d-value increases with the increase of the impact velocity. To examine possible correlation of this feature with nitrogen content, elemental analyses (C, H, and N) for several products were carried out on SUMIGRAPH Model NCH-21. The sample was subjected to oxygen circulating combustion system at 850 °C. Carbon, hydrogen, and nitrogen were detected as CO$_2$, H$_2$O, N$_2$ respectively with thermal conductivity detector. Acetanilide (Kishida Chemical, C, 71.072 wt% (R(range) = 0.050 wt%); H, 6.737 wt% (R = 0.044 wt%); N, 10.348 wt% (R = 0.021 wt%)) was used as standard. The results disclosed that the atomic ratio of nitrogen to carbon (N/C) decreased with the increase of the impact velocity. Apparently, the more severe the shock condition, the lower the nitrogen content of the product. Thus, the product of the highest nitrogen content (N/C = 1.26) was obtained when the reactants were shocked at the impact velocity of 0.890 km/s whereas the shock experiment at the highest impact velocity (1.50 km/s) afforded the product of the lowest nitrogen content (N/C = 0.427) with the largest d-value (0.336 nm). The total weight percent for C, H, and N (76.1–87.8 wt%) is indicative of existence of another atomic component. Elemental analysis for oxygen was executed on LECO Nitrogen/Oxygen Analyzer TC-436. Combustion of the sample was performed with impulse furnace at 3000 °C. Oxygen was detected as CO$_2$ with infrared rays detector. Y$_2$O$_3$ (Shin–Etsu Chemical, 99.999%) was used as standard. As shown in Table 1 significant amounts of oxygen contaminated the samples presumably as a result of oxidation after opening the sample containers, because doubly treated samples (#1172 and #1175) indicated highest oxygen contents. There seems to be two groups with respect to hydrogen content in products. Hydrogen-rich products were obtained at relatively low impact velocities below 1.2 km/s, but indicate no correlation with the oxygen content. The reasons for the very low hydrogen contents are unclear at present.

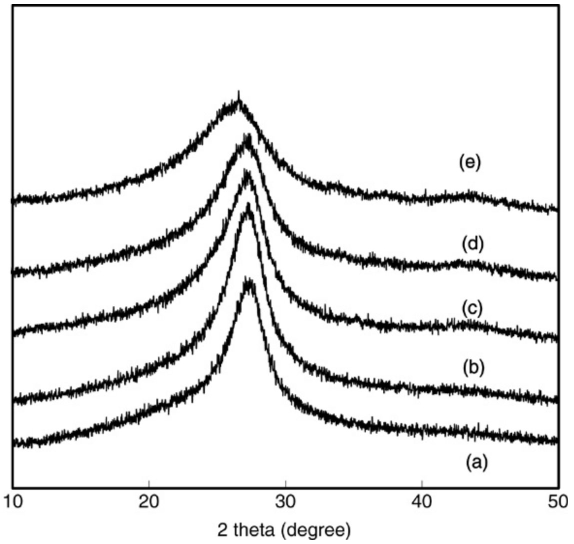

Fig. 2. Comparison of XRD patterns of samples 1177 (a), 1178 (b), 1170 (c), 1172 (d), and 1176 (e). See Table 1 for the shock conditions, d-values and elemental analyses.

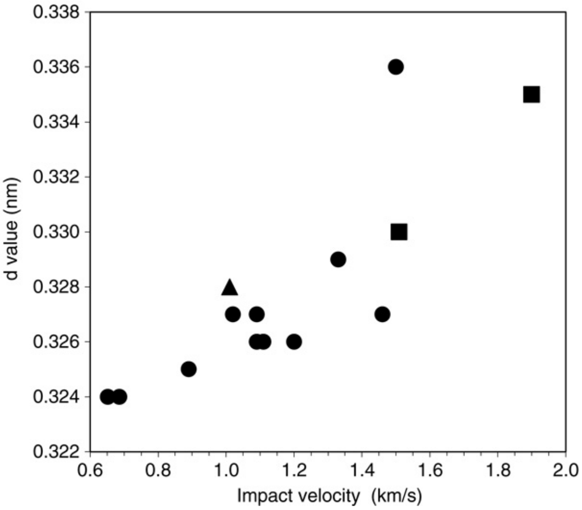

Fig. 3. Plot of d-value versus impact velocity. The filled circles, squares, and triangle represent the results for the 11 shots (× = Br), the 2 shots (1172, 1176), and the shot 1196 in Table 1, respectively.

According as the shock condition became harsher, nitrogen would escape from the carbon nitride material, driving

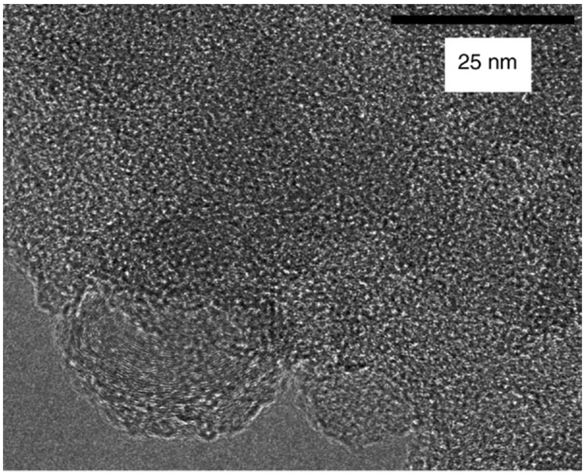

Fig. 4. High-resolution TEM image of amorphous carbon nitride produced in shot 1175.

its composition and structure closer to graphite ($d_{002} = 0.335$ nm). To confirm the nitrogen escape, the products obtained in #1164 and #1165 were exposed to the shock condition. After the sample was mixed with 90 wt% Cu powder in an agate mortar, the mixture was ground with an agate pestle for 5 min. and put into the sample container (Cu). Preparation of the sample container was according to the same method as described above. The densities (g/cm^3) of the samples were evaluated as 5.7 (#1172) and 6.6 (#1176). A large excess of copper powder enhances the shock condition due to greater shock impedance relative to the sample without copper. After shock treatment the product was collected from the recovered sample container and suspended to HNO_3aq (13 N, 50 mL). The precipitates were washed with distilled water (rt), dried at 120 °C with silica gel, and subjected to XRD measurement and elemental analysis. The results were described at #1172 and #1176 in Table 1.

Samples #1175 and #1179 were investigated by transmission electron microscopy (TEM) coupled with EDX analysis. Both samples indicated significant amounts of bromine and copper, heterogeneously distributed, and no sodium. Fig. 4 shows a typical TEM image of sample #1175. It consists of disordered lattice images mostly and very limited areas such as the left-bottom portion in Fig. 4 display partial ordering similar to layered structures. These results explain that samples are contaminated by CuBr probably covered with amorphous C–N material.

The XRD spectra (Fig. 2(d), (e)) of the acquired black powder were similar to the starting materials though the location of the strongest peak shifted larger ($d = 0.330$ nm ($v_{\mathrm{imp}} = 1.51$ km/s) and $d = 0.335$ nm ($v_{\mathrm{imp}} = 1.90$ km/s)) compared with that in #1180 ($d = 0.326$ nm) and #1165 ($d = 0.329$ nm). Increase in half width of the peak with the increase in the impact velocity as exampled in Fig. 2 is probably due to structural disorder caused by partial nitrogen abstraction from the C–N network. These results imply release of nitrogen from the starting materials. In fact nitrogen content of the products was proven to be much lower (N/C = 0.602 ($v_{\mathrm{imp}} = 1.51$ km/s) and even 0.382 ($v_{\mathrm{imp}} = 1.90$ km/s)) than that in #1180(N/C = 0.955 ($v_{\mathrm{imp}} = 1.20$ km/s)).

Finally, the shock-recovery experiment for the mixture of CI_4 and $NaN(CN)_2$ was examined (#1196 in Table 1). In the XRD spectrum (10–110°) of the product before treatment with acid and water, the strongest set of 14 peaks is attributable to CuI. The second strongest set of 30 peaks corresponds to $NaI2H_2O$. Formation of CuI is suggestive of generation of I_2 in the reaction process. CI_4, $NaN(CN)_2$, and the trimer of $NaN(CN)_2$ were significantly not recognizable. After the product was suspended in HNO_3aq (13 N, 50 mL), the precipitates were washed with distilled water (rt and then 60 °C) and dried at 120 °C with silica gel. The shape and position of the peak in the XRD spectrum of the product were essentially unaltered although the yield was doubled compared with that in the experiments for CBr_4 and $NaN(CN)_2$.

In conclusion, nitrogen-rich carbon nitride materials with N/C up to 1.26 have been successfully prepared from CX_4 (X = Br, I) and $NaN(CN)_2$ by shock synthesis. Obviously, exposure of the materials at elevated temperatures should be avoided for further transformation to a predicted metastable phase without release of nitrogen. Investigation along this line is currently in progress.

Acknowledgements

This work was supported in part by a Grand-in Aid for Exploratory Research. K.S. acknowledges support by NIMS for his stay. K.S. is grateful to Professor A. Sawaoka for encouragement. Elemental analyses of C, H, and N were performed by Sumika Chemical Analysis Service. The authors thank Mr. Y. Yajima and K. Kurashima in Ceramics Analysis Group, NIMS for elemental analysis of oxygen and analytical TEM, respectively.

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