

Powder Synthesis and Characterization of Amorphous Carbon Nitride

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Received April 20, 2000. Revised Manuscript Received July 14, 2000

Carbon nitride powder has been prepared by solid-state reaction between cyanuric chloride or its fluoro analogue and lithium nitride. The determined, by elemental analysis, atomic N/C ratio (1.33) in the synthesized material is entirely consistent with the C_3N_4 stoichiometry. Combined material characterization data, obtained by Fourier transform infrared, Raman, UV–visible, (^{13}C) magic-angle spinning NMR, X-ray photoelectron spectroscopy, thermal gravimetric analysis/differential thermal analysis, and pyrolysis–electron ionization mass spectrometry methods, provide substantial evidence for graphite-like sp^2 -bonded structure composed of building blocks of s-triazine rings bridged by the 3-fold coordinated nitrogen atoms in the bulk carbon nitride. As indicated by X-ray and scanning electron microscopy analytical data, the material is amorphous and changes from turbostratic to more ordered layered graphitic morphology under high pressures. The availability of stoichiometric carbon nitride α - C_3N_4 in gram quantities, made possible by a developed low-cost synthetic method, facilitates the extensive studies of bulk processing and electromechanical properties, and high-pressure/high-temperature transformations of this material into superhard crystalline polymorphic phases.

Introduction

The preparation of binary, ternary, and quaternary carbonitride materials, such as C_3N_4 , B–C–N, Al–C–N, Al–B–C–N, Si–B–C–N, etc., is an area of significant current interest. These non-oxide lightweight materials are expected to possess a combination of extreme hardness, oxidation resistance, and chemical inertness.^{1–10} The most exciting material in this family is the carbon nitride designated as β - C_3N_4 , for which a hardness challenging that of diamond is predicted.^{1–3} In addition to a potentially superhard β -phase, the existence of α -, cubic, pseudocubic and graphitic polymorph phases of carbon nitride have been recently suggested on the basis of calculations^{11,12} and experiments.^{13,14} Numerous experimental attempts to synthesize the β -form of carbon nitride have exploited various chemical and physical thin films deposition techniques,¹⁵ have ended up with predominantly amorphous

materials possessing nitrogen contents much lower than the expected 57 atom % for C_3N_4 (except for the thin films prepared from single-source precursors by Kouvetakis et al.).¹⁶ The observation of small α - C_3N_4 and β - C_3N_4 or cubic C_3N_4 crystallites embedded in an amorphous carbon nitride film was reported by several groups.^{15,17–21} However, serious doubts that these potentially superhard materials were actually made will remain until large crystals of carbon nitride are synthesized and precisely characterized and their mechanical properties are tested. As a summary, it has been suggested on the basis of the large amount of experimental results available so far that physical deposition methods are unable to yield the crystalline hard material.^{20,22}

The difficulties in the synthesis of hard carbon nitrides are very likely related to their low thermodynamic stability with respect to the elements (C and N_2), indicated by a positive values of enthalpies of formation.²³ The synthesis at high pressures and high temperatures may offer a more promising route to achieve this goal, in view of reported successes in high-pressure synthesis of sp^2 -bonded carbon nitride by Badding and co-workers^{23,24} and Weill and co-workers¹⁴ and microme-

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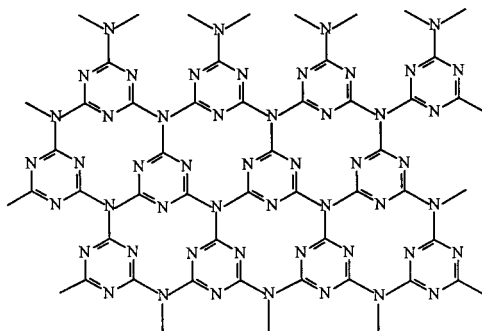
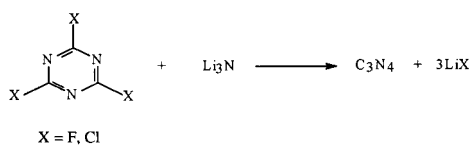


Figure 1. sp^2 -Bonded structure of carbon nitride, α - C_3N_4 .

ter-sized α - C_3N_4 and β - C_3N_4 crystals by the Chinese team.²⁵ The LDA calculations predict that sp^3 -bonded β - C_3N_4 phase is only about 20 kJ/mol less stable than sp^2 -bonded carbon nitride. This implies that, similar to the graphite/diamond and h-BN/c-BN transformations under high-pressure/high-temperature conditions, the crystalline sp^3 -bonded carbon nitride can be synthesized from the sp^2 -bonded graphite-like carbon nitride.

The syntheses of large crystals of β - C_3N_4 as well as other polymorphs appear to be very promising if the bulk quantities of stoichiometric sp^2 -bonded carbon nitride as precursor are at hand. With this aim in view, we have recently succeeded in solid-state synthesis of carbonitride powders in gram quantities. The use of cyanuric chloride, $C_3N_3Cl_3$, and its fluoro analogue, $C_3N_3F_3$, as an sp^2 C=N precursors and of lithium nitride Li_3N as a nitridation and cross-linking agent have proven to be efficient in the syntheses of nitrogen-rich carbonitride powders. These reactions are most likely to result in the 3-fold N-bridged s-triazine ring structure (Figure 1) and to proceed according to the following general scheme:



The choice of these synthetic routes was influenced by known successful preparation of nitrides of lanthanides and transition metals through solid-state metathesis reactions such as $MCl_n + Li_3N \rightarrow MN + LiCl$ ^{26,27} and of gallium nitride by solvothermal reaction of $GaCl_3$ and Li_3N .²⁸ The additional motivation was the commercial availability and low cost of starting materials $C_3N_3X_3$ and Li_3N .

Experimental Section

General Procedures. Cyanuric chloride (99%, Sigma/Aldrich) was sublimated twice in a vacuum before use. Cyanuric fluoride (99%, Alfa) and lithium nitride (99.5%, Strem) were used as received. The small-scale reactions were carried out in a sealed thick-wall Pyrex glass ampules. The

larger scale syntheses were performed in a closed stainless steel or Monel tube reactor.

In a typical example of these experiments, 2214 mg (12 mmol) of $C_3N_3Cl_3$ and 630 mg (18 mmol) of Li_3N fine powders were mixed together in a N_2 -filled drybox and loaded into a stainless steel reactor, which afterward was sealed with a leak-tight con-flat cap. The reactor was taken out of the drybox and suspended in a vertical furnace by a sample holder of an air-driven vibrator, which was kept in operation until the end of reaction. The furnace temperature was gradually and slowly raised to about 380 °C, held for 2–4 h, and then brought back to room temperature. After the reaction, byproduct $LiCl$ was removed by washing with water on a 0.2 μm Cole-Parmer PTFE filter membrane, and the remaining dark-brown product was dried overnight at about 100 °C under vacuum; the obtained powder weighed 1092 mg (98.5% of that theoretically expected for C_3N_4). A microprobe analysis shows that the powders prepared by the described method are nitrogen-rich with the following varying compositions: $C_{0.37-0.42}N_{0.55-0.58}O_{0.02-0.05}Cl_{0.002-0.005}$.

The same reaction proceeded faster (about 0.5 h) and at lower temperature (300 °C) in a Monel reactor; however, the obtained orange-colored powder has contained up to 2–5 atom % Cl. A similar product was prepared when the synthesis was carried out in a sealed glass tube, yet with a significantly lower yield and much longer reaction time (24 h). This strongly suggests a catalytic effect of transition metals (Fe, Ni, Cu) on the reaction.

Materials Characterization. The Fourier transform infrared (FTIR) spectra of the carbon nitride powders pressed into a KBr pellet were collected on a Perkin-Elmer Paragon 1000 FTIR spectrometer with 1 cm^{-1} resolution. Raman spectroscopy measurements for the powders placed on top of a standard microscope slide were carried out on a Renishaw System 1000 micro-Raman spectrometer with an 1800 line/mm grating and a 514.5 nm Ar ion laser. UV-Vis spectra were recorded on a GBC UV/vis 918 spectrophotometer. Quantitative elemental analyses were performed with the Cameca SX-50 electron microprobe analyzer equipped with PGT energy-dispersive spectrometer (EDS) and the following parameters: acceleration voltage of 15 kV, beam current of 15 nA, beam diameter of 20 μm , and peak and background counting time of 20 s. X-ray photoelectron spectroscopy (XPS) data were collected on a Physical Electronics PHI 7500 X-ray photoelectron spectrometer with an Al $K\alpha$ radiation source (1486.6 eV), a power setting of 350 W, and an analyzer pass energy of 23.5 eV. ^{13}C magic-angle spinning (MAS) NMR spectra of powders packed into a 7 mm rotor were recorded on a Bruker Instruments 200 MHz spectrometer with a 90° pulse width of 4 μs and relaxation delay of 10 s and referenced to the ^{13}C chemical shift of glycine carbonyl at 176.2 ppm. Thermal gravimetric analyses (TGA) were done with a TA Instruments TGA-DTA 2960 analyzer. Pyrolysis-mass spectrometry (MS) data were obtained with the Finnigan-MAT 95 mass spectrometer. Scanning electron microscopy (SEM) was carried out on a Jeol model JSM-6320F field emission microscope at 30 keV beam energy. X-ray diffraction data were collected on a Siemens powder diffractometer with a Cu $K\alpha$ radiation source.

The disk-shaped specimens of carbon nitride were fabricated by cold isothermal pressing at 55 000 psi of the pellets sealed into a latex bag. Prior to that procedure, the pellets were prepared from a powder placed into a hardened steel die and densified at 5000 psi for 5 min. Electric conductivity measurements were performed on disk-shaped ceramic samples by a four-point method.

Results and Discussion

The orange or dark-brown colored powders, isolated after complete removal of the reaction byproducts, $LiCl$ or LiF , did not melt at temperatures up to as high as 400 °C and also did not dissolve in common organic solvents, hinting at a high-molecular nature of synthesized materials. Solvation at some degree (about 10–

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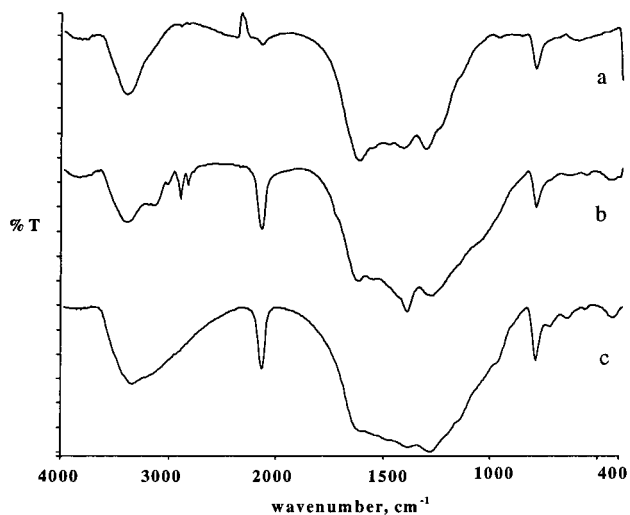


Figure 2. FTIR spectra of (a) $a\text{-C}_3\text{N}_4$ powder synthesized in a Monel reactor at 300 °C, (b) the same material annealed to 650 °C, and (c) powder synthesized in stainless steel reactor at 380 °C.

20 mg/L) was achieved for finely ground powder by sonication in water or alcohol, which produced a clear light-yellow solution, stable to precipitation for hours. According to elemental analyses (Galbraith Laboratories, Inc.), the overall N/C atom % ratio in the prepared powders was approximately 1.33, which is in agreement with the C_3N_4 stoichiometry. Besides carbon and nitrogen, the analyses have yielded about 0.7 wt % hydrogen content in the samples. The electron microprobe studies of powders also revealed that they contain 2–4 atom % oxygen and only trace amounts of halogens (Cl or F). These data thus indicate the likely presence of OH, NH, and NH_2 functional groups in the polymer structure of powders studied.

The FTIR spectra of these newly synthesized carbon nitride bulk materials have shown the features very similar to those of nitrogen-rich carbonitride thin films, observed earlier by us²⁹ and other research groups.^{16,30,31} The spectrum of orange powder (Figure 2a) shows broad bands of the stretching and deformation modes of NH_2 groups at 3424 and 1627 cm^{-1} (as well as an overlapping band of OH stretching), weak band at 2162 cm^{-1} due to the cyano group stretch, and a group of multiple bands characteristic for s-triazine ring vibrations, at 1561 cm^{-1} (quadrant stretch), 1490 and 1421 cm^{-1} (double semicircle stretchings), and 805 cm^{-1} (out-of-plane ring bending by sextants).³² The strong band observed in this spectrum at 1314 cm^{-1} characterizes the C–N stretch in the 3-fold N-bridge linking the triazine rings. The NH bridge-coupled triazine rings are also likely to be present, as well as terminal NH_2 and NHCN groups.

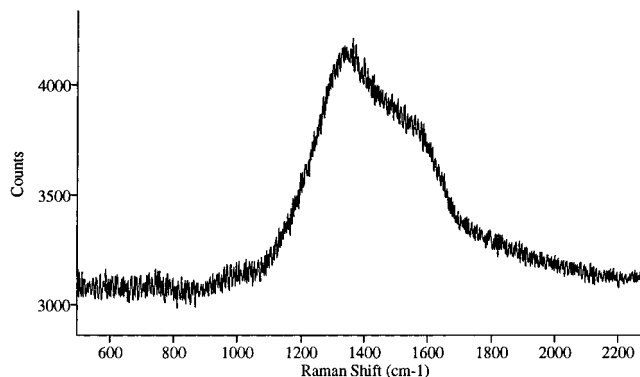


Figure 3. Raman spectrum of $a\text{-C}_3\text{N}_4$ powder.

They are likely to induce loss of the 3-fold axis of symmetry in the polymer structure (Figure 1) and result in the appearance of double bands in the spectrum, e.g., an already mentioned band of semicircle ring stretch at 1490 cm^{-1} and a band of double ring quadrant stretch at about 1580–1600 cm^{-1} , which is overlapped by a strong NH_2 deformation band (Figure 2). Annealing of the powders to 650 °C in a vacuum caused an increase of absorption of the $\text{C}\equiv\text{N}$ group at 2162 cm^{-1} and reduction of intensities of bands of NH_2 and N–C vibrations at 3424, 1627, and 1314 cm^{-1} , respectively, in the FTIR spectra (Figure 2b) due to a loss of ammonia probably accompanied by a partial rearrangement and destruction of s-triazine rings under high temperatures, as observed earlier for melamine polymerization products.^{33–36} Since somewhat similar secondary processes are likely to take place during the carbon nitride preparation in a stainless steel reactor, proceeding at a higher reaction temperature than in the Monel reactor, the spectrum of the obtained powder (Figure 2c) shows as strong absorption of the cyano group at 2162 cm^{-1} as the spectrum of annealed material (Figure 2b).

A typical Raman spectrum of carbon nitride powder (Figure 3) shows two broad peaks with maxima at about 1340 and 1545 cm^{-1} , corresponding to D and G Raman bands of amorphous graphitic carbon, respectively. The locations of these peaks resemble those typically observed for carbon nitride thin films of an average C_2N composition;^{37–39} however, unlike them, in the Raman spectra of $a\text{-C}_3\text{N}_4$ powder, due to a much higher nitrogen content, the D band appears to be significantly stronger than the G band.

The presence of triazine rings in the $a\text{-C}_3\text{N}_4$ polymer structure is also evidenced by UV–vis studies of a light-yellow solution produced by sonication of carbon nitride powder in water. The observed strong absorption at 250 nm (Figure 4) lies in the range characteristic for $\pi\text{-}\pi^*$ electronic transition in the aromatic 1,3,5-triazine compounds.⁴⁰ Additional absorption, very broad and weak,

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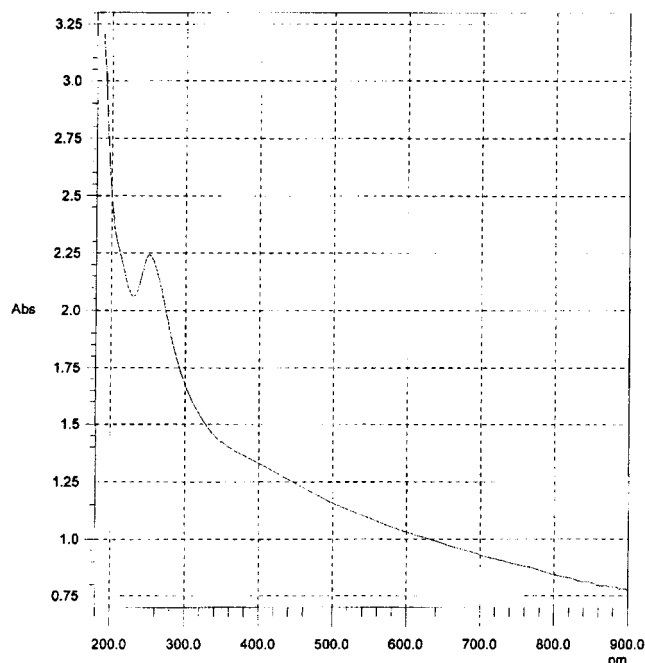


Figure 4. UV-Vis spectrum of light-yellow colored water solution of carbon nitride.

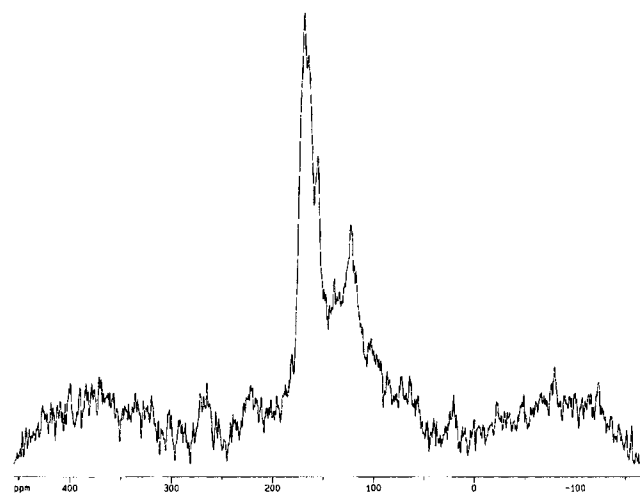


Figure 5. ^{13}C MAS NMR spectrum of $a\text{-C}_3\text{N}_4$ powder.

was observed in the visible region at about 410 nm. Presumably, it belongs to the $n\text{-}\pi^*$ transitions involving lone pairs of nitrogen atoms in the polymer.

The solid-state (^{13}C) MAS NMR spectrum (Figure 5) exhibited two broad peaks: the larger at 168.9 ppm (with two shoulder peaks at 165.3 and 155.7 ppm) corresponding to the sp^2 -hybridized carbon atoms from the s -triazine rings and the smaller at 123.4 ppm for the sp carbon of the cyano group.^{40,41} According to this spectrum and the FTIR spectral data for nonannealed carbon nitride powder, there are practically no hydrogen atoms bonded to carbon atoms present in the polymer structure. The s -triazine ring carbon peak positions in the NMR spectrum are found to lie close to those

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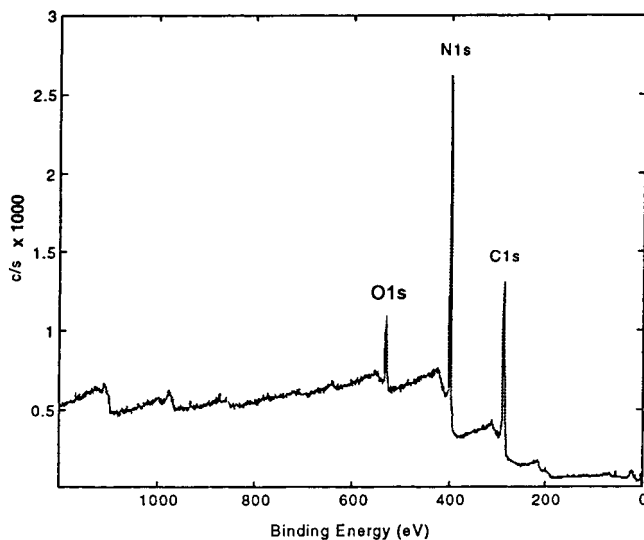


Figure 6. XPS survey scan of $a\text{-C}_3\text{N}_4$ powder.

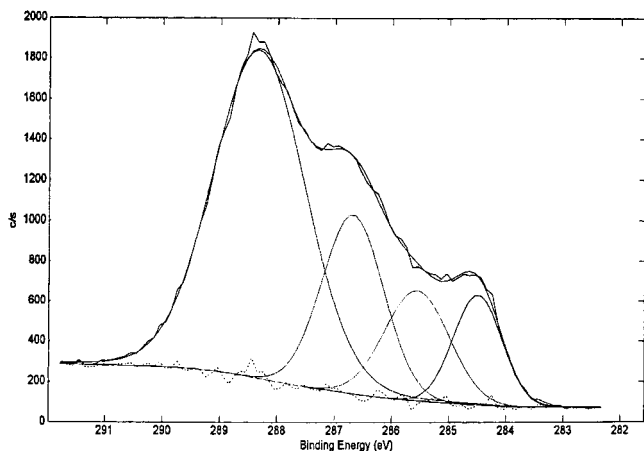


Figure 7. Deconvolution of C1s peak in the high-resolution X-ray photoelectron spectrum of $a\text{-C}_3\text{N}_4$ powder.

reported for B–C–N powder synthesized from melamine and BCl_3 and being similarly composed from layers of triazine rings bridged by NH groups and nitrogen and boron atoms.³⁵ At the same time, these and our NMR data do not agree with the earlier (^{13}C) NMR spectra, observed by Kouvatakis et al.,¹⁶ of free-standing films of C_3N_4 stoichiometry, which exhibited two resonance peaks at much higher field, at 104 and 115 ppm. These peaks were also assigned to sp^2 hybridized carbons in the proposed nitrogen-bridged s -triazine ring structure, identical to that we suggest for $a\text{-C}_3\text{N}_4$ powder in the present work (Figure 1). Due to the large discrepancy in these data, it is not easy to agree with the structure proposed earlier for the C_3N_4 film.¹⁶

The XPS data support the results obtained by FTIR, UV-vis, and NMR spectroscopy. In the XPS survey spectrum, given in Figure 6, three observed peaks indicate that synthesized material is composed primarily from carbon and nitrogen; however, some oxygen impurity of about 5% is also present. Higher resolution XPS data, referenced to a peak at 284.6 eV of graphite powder taken as a standard, show that the C and N lines can be split and deconvoluted. The C1s peak (Figure 7) deconvolves into four components at binding energies of 284.5, 285.5, 286.6, and 288.1 (major component) eV, which are attributed to the C–C, C–O,

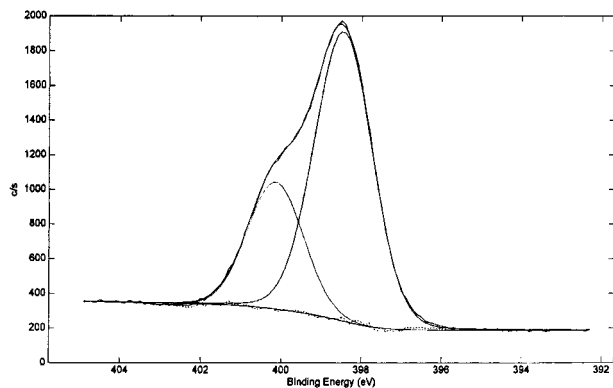


Figure 8. Deconvolution of N1s peak in the high-resolution X-ray photoelectron spectrum of $a\text{-C}_3\text{N}_4$ powder.

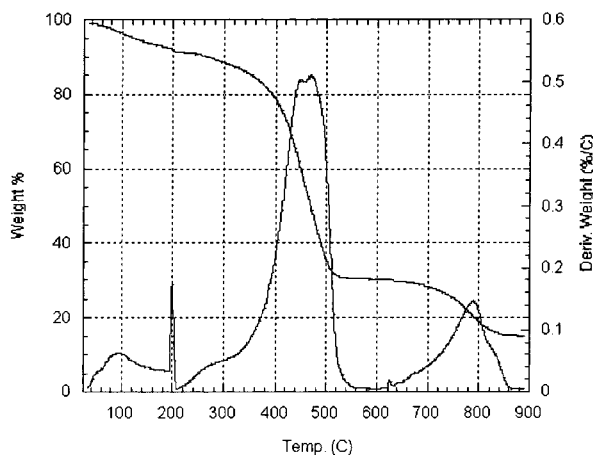


Figure 9. TGA/DTA data plot for carbon nitride in air.

$\text{C}\equiv\text{N}$, and $\text{C}=\text{N}$ bonds, respectively. The C–C peak originates from graphitic carbon, presumably formed during minor decomposition of the carbon nitride sample under X-ray irradiation. The deconvoluted N1s peak (Figure 8) shows a major component at 398.5 eV due to nitrogen, sp^2 -bonded to carbon, and a shoulder peak at a higher binding energy, 400.1 eV, assigned to sp -bonded nitrogen in the terminal $\text{C}\equiv\text{N}$ groups.^{29,30,42} The XPS data thus strongly suggest that the graphite-like sp^2 -bonded structure (Figure 1) is most likely for the carbonitride powders.

These observations also agree with the TGA/differential thermal analysis (DTA) and vacuum pyrolysis–MS analyses. The TGA/DTA data plots for carbon nitride powder are shown in Figures 9 and 10. They show that this material is significantly less thermally stable in air (Figure 9) than in an inert atmosphere (Figure 10), undergoing stepwise decomposition in both cases. Major weight loss in argon is observed at temperatures above 550 °C, in comparison with the 400 °C on air. According to mass spectral study of evolution products, in which only ions with mass numbers (m/z) higher than 35 were detected (Figure 11), the mass loss above 450 °C is in part due to cyanic acid HOCN ($m/z = 43$) and most likely ammonia, as evidenced by FTIR studies of annealed material at similar temperatures (Figure 2b). At a higher temperatures (up to 900 °C) the evolution of other species, detected by the mass fragments at $m/z = 52$ (C_2N_2^+), 64 (C_3N_2^+), 78 (C_3N_3^+), and 92 (C_3N_4^+), were observed as well. These data provide clear evidence for formation of cyanogen (CN)₂

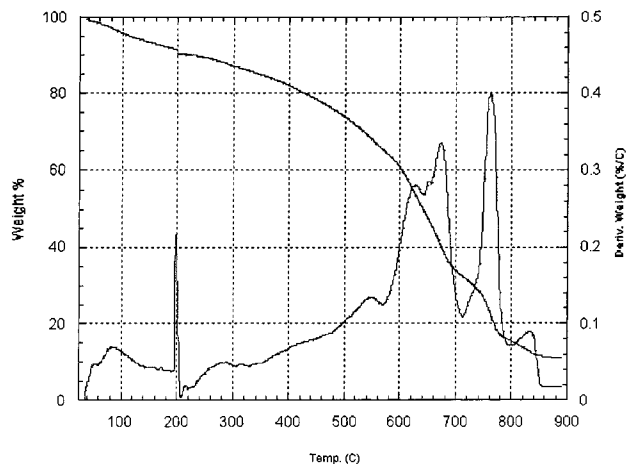


Figure 10. TGA/DTA data plot for carbon nitride in argon.

and heavier C_3N_x species as a result of fragmentation of triazine rings being a major unit in the suggested polymer structure of $a\text{-C}_3\text{N}_4$ material.

All synthesized $a\text{-C}_3\text{N}_4$ powders are amorphous; therefore, only a very broad reflection centered at about 3.0 Å could be detected in X-ray diffraction (XRD) measurements. These data do not look like the XRD patterns of the carbon nitride synthesized, according to Kawaguchi et al.,⁴³ from similar reagents ($\text{C}_3\text{N}_3\text{Cl}_3$ and Li_3N) but under reaction conditions which differ from those we used in our work. On the basis of diffuse reflectance UV–vis spectra of the powder, the optical band gap for $a\text{-C}_3\text{N}_4$ material was estimated to be approximately 3.1 eV. We were able to perform densification of micronized C_3N_4 powders by cold isothermal pressing at pressure of 55 000 psi. The disk-shaped ceramics formed had densities of about 1.34–1.38 g/cm^3 , being much lighter than graphite ($d = 2.25 \text{ g}/\text{cm}^3$). The linear electric resistivities of these ceramics, measured at about 0.67 $\text{M}\Omega\cdot\text{cm}$, lie close to those of blue diamond semiconductors. Because of wide band gap semiconducting properties, the undoped and doped carbon nitride ceramics require testing for possible application as secondary electron emitters. Besides that, the ceramic disks of $a\text{-C}_3\text{N}_4$ could be studied for application as targets for laser ablation in the deposition processes of potentially ultrahard C–N films.

Finally, based on availability of *stoichiometric* sp^2 -bonded carbon nitride as a result of present work, we have carried out a series of high-pressure experiments in pursuit of large crystals of superhard $\beta\text{-C}_3\text{N}_4$ and other predicted polymorphs with amorphous $a\text{-C}_3\text{N}_4$ powder as a precursor. According to SEM (Figure 12), EDAX, micro-Raman, and powder X-ray studies, under pressures of 8–12 GPa the structure of carbon nitride changes in the direction from an amorphous one (Figure 12A) to more ordered layered graphite-like structure with interplane d spacing of about 3.0–3.1 Å, retaining the C_3N_4 stoichiometry at temperatures of up to 400 °C (Figure 12C). The TEM studies, however, did not reveal the presence of any (nano- or micro-) crystalline phases of carbon nitride, which means that the material still

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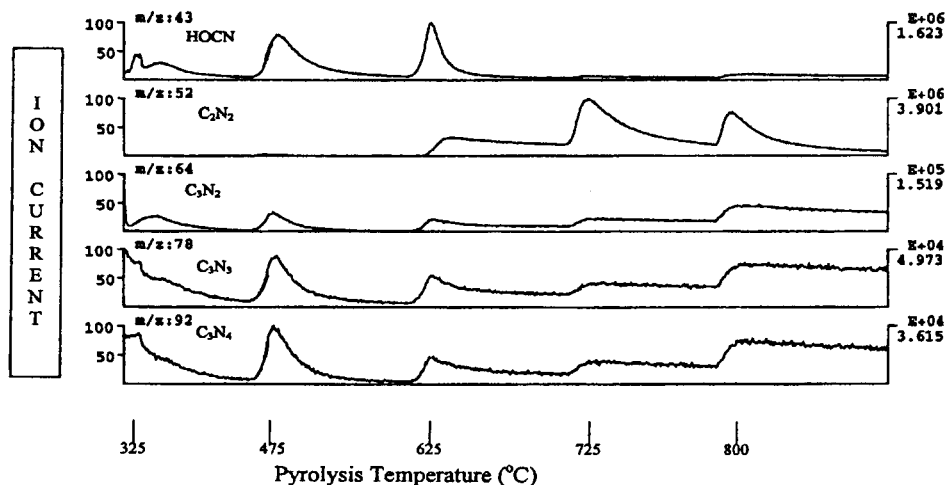


Figure 11. Electron ionization mass spectra of the evolution products of stepped pyrolysis of $a\text{-C}_3\text{N}_4$ carbon nitride polymer at variable temperatures.

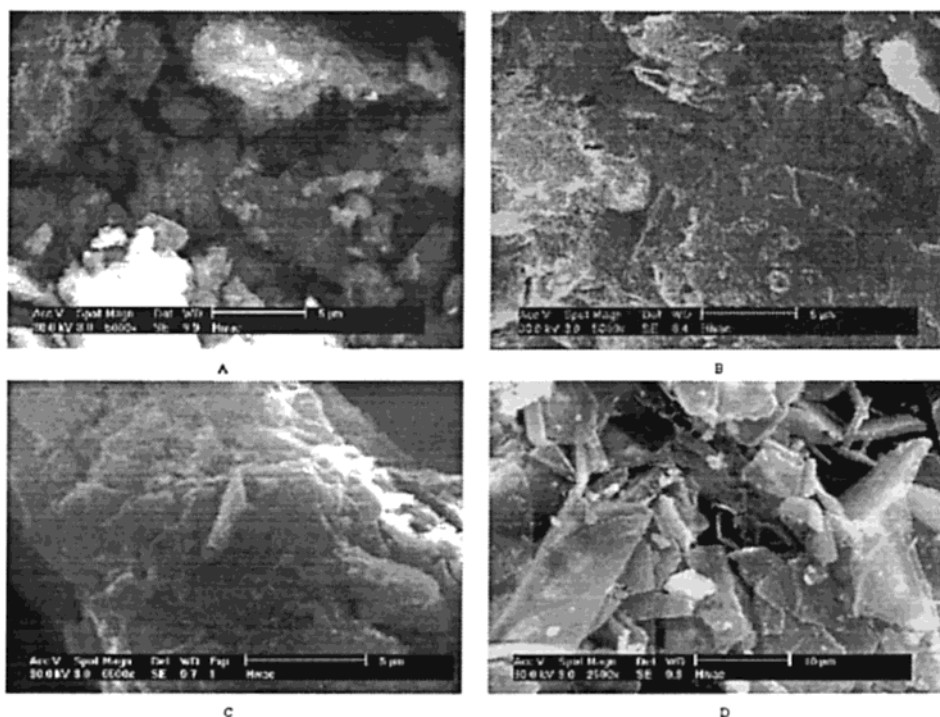


Figure 12. Scanning electron micrographs: (A) $a\text{-C}_3\text{N}_4$ powder precursor; (B) densified material obtained after exposure of powder to high pressure of 8 GPa at room temperature; (C) material obtained from powder after exposure to high pressure of 12 GPa at temperature of 400 °C; and (D) pure carbon graphite material formed from powder after exposure to high pressure of 8 GPa at a temperature of 1200 °C.

remains amorphous although well densified under pressure. This material loses nitrogen at higher temperatures (up to 1200 °C) to convert into a pure carbon phase of graphite with d spacing of 3.34 Å (Figure 12D). These preliminary experiments allowed us to determine so far the temperature range where the phase transformation of carbon nitride starts to occur without change of the C_3N_4 composition. The formation of crystalline phases, predicted to be superhard, probably will require application of higher pressures than those tested so far or catalysts, and these experiments are in progress.

Conclusion

The powder synthesis of amorphous carbon nitride with a stoichiometry very close to C_3N_4 in gram quantities has been achieved in the present work. The dem-

onstrated approach, which is based on fast solid-state reactions, is particularly attractive since (i) it uses relatively cheap reagents and does not require synthesis of single-source precursors, as in the previously reported preparation of carbonitride,^{16,44,45} (ii) it produces powders with a higher nitrogen content than, for example, the carbon nitride powders of approximately C_4N_5 stoichiometry described in a German patent,⁴⁵ (iii) the reaction routes, leading to production of covalently bonded not only binary but also ternary and quaternary carbonitride materials with controlled stoichiometry, morphology, and mechanical and electric properties can

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probably be designed. We have recently verified the flexibility of this approach by successful synthesis of amorphous B–C–N powders of approximate $B_3C_3N_7$ stoichiometry, and extended our current work to preparation of other carbo-nitride materials.

Acknowledgment. We thank the Center for Nanoscale Science and Technology at Rice University for providing access to their materials characterization facilities. Thanks are also extended to Dr. L. Alemany for running the (^{13}C) MAS NMR spectra, Mr. M. Pierson for performing the electron microprobe analyses, and Professor W. Wilson for electrical conductivity measurements. Dr. Paul Van der Heide, at the Department of Chemistry, University of Houston, is thanked for help

with the XPS characterization of carbon nitride materials. The collaboration of Professor K. Salama and Mr. G. Majkic, at the Department of Mechanical Engineering, University of Houston, in cold isothermal pressing of carbon nitride powders is gratefully acknowledged. We are also grateful to Professor Dr. E. N. Yakovlev and co-workers at the High Pressure Physics Institute of the Russian Academy of Sciences for performing a series of preliminary high-pressure/high-temperature experiments. The financial support from MarChem, The Robert Welch Foundation, and U.S. Army Research Office Grant DAAH04-96-1-0307 to Rice University are greatly appreciated.

CM000328R