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Rapid, facile synthesis of nitrogen-rich carbon nitride powders

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There is increasing interest in high surface area carbon nitride materials as potential coordinatively active analogs of amorphous carbon systems. It is generally difficult to produce extended carbon structures with high nitrogen contents. This article describes a facile molecular decomposition process that produces bulk quantities of an amorphous nitrogen-rich carbon nitride material, C_3N_{4+x} where $0.5 < x < 0.8$, in only a few seconds without the use of complex experimental apparatus. The trichloromelamine molecular precursor $[(C_3N_3)(NHCl)_3]$ rapidly decomposes when heated externally above 185 °C or when brought into contact with a heated filament. Morphological studies show that the rapid synthesis process produces a porous, sponge-like material containing spherical nanofeatures (<300 nm). These amorphous carbon nitrides were analyzed by IR, NMR, optical, and X-ray photoelectron spectroscopy, which indicate that the carbon centers have primarily sp^2 hybridization, triazine (C_3N_3) rings are retained in the product, and nitrogen species bridge triazines. These C_3N_{4+x} materials are also luminescent in the blue region even after annealing to 400 °C. They exhibit thermal and chemical stability with no significant decomposition until 600 °C or reactivity with concentrated aqueous base.

Introduction

While silicon nitride (Si_3N_4) is a stable, high-temperature ceramic and other Group 14 compounds with large nitrogen contents have been synthesized (*e.g.*, Ge_3N_4 and Sn_3N_4),[1] analogous nitrogen-rich *carbon* nitrides are rare. A theoretical treatment predicted diamond-like hardness for an sp^3 carbon nitride phase (C_3N_4 or $CN_{1.33}$) with the β-Si_3N_4 structure[2] and spurred a considerable number of research efforts over the past decade. The theoretical stability of various layered (sp^2) CN_x structures has been examined[3] and polymeric C_3N_4 materials may potentially convert to dense three-dimensional structures under pressure.[4] Carbon nitrides with sp^2 or sp^3 bonded carbon may find practical uses similar to their all-carbon counterparts, which have utility as hard coatings,[5] lithium intercalation electrodes,[6] metal catalyst supports,[7] and hydrogen storage materials.[8] The growth of carbon nitride films has generally been accomplished by elemental gas phase processes producing films with low to moderate nitrogen contents, *e.g.* $CN_{0.2}$ to $CN_{1.0}$.[9] Early molecular routes to bulk CN_x solids required high temperatures (>700 °C) and resulted in nitrogen poor materials, *e.g.*, $CN_{0.17}$ from pyridine (C_5H_5N) and Cl_2.[10] The catalyzed high-temperature pyrolysis of melamine $[(C_3N_3)(NH_2)_3]$ or pyridine was also recently demonstrated to produce aligned nitrogen-doped carbon nanotubes (<10 at% N).[11]

Low-temperature molecular precursor routes have been proposed as potential routes to metastable high-nitrogen content carbon nitrogen networks[12] and precursors with direct C–N bonds were concluded to be essential to carbon nitride synthesis.[13] There are a few examples of exotic carbon nitride precursors and relatively complex decomposition routes that have been utilized to access bulk CN_x solids with high nitrogen contents ($x > 1$). Selected examples using a triazine ring (C_3N_3) structural motif include: 1) the pyrolysis and shock compression of triazine $[(C_3N_3)H_3]$ and various derivatives to produce materials with 10 to 50 at% nitrogen;[14,15] 2) the solvothermal reaction between $(C_3N_3)(NH_2)_3$ and $(C_3N_3)Cl_3$ in ethylenediamine at 250 °C and >1000 atm to yield $C_3N_4(H)_2$ powders;[16] 3) the vapor deposition of $[(Me_3Si)_2N](C_3N_3)Cl_2$ at 400 °C to grow graphitic C_3N_4 films;[17] and 4) the solid-state reaction between $(C_3N_3)Cl_3$ and Li_3N at 380 °C also produces bulk C_3N_4 powders.[18] We previously demonstrated that an energetic solid, $(C_3N_3)(N_3)_3$, slowly decomposes at 185 °C to yield C_3N_{4+x} ($x \leqslant 0.7$) materials,[19] however this precursor's thermal instability makes it challenging to prevent rapid decomposition to elemental nanocarbon structures.[19,20] Of particular note, a recent high-pressure decomposition of $(C_3N_3)(NH_2)Cl_2$ at 500 °C produced a crystalline polymeric $[C_3N_{4.5}H_{1.5}\cdot 0.5HCl]$ compound with triazine rings bonded to each other through secondary amine bridges and chlorides residing in interstitial spaces.[21] Another study on the Lewis acid catalyzed decomposition of $(C_3N_3)(NH_2)_3$ at 650 °C reports a crystalline solid with a $C_3N_{4.3}H_{1.0}$ composition.[22]

In this article we detail the one-step synthesis of nitrogen-rich carbon nitrides near a C_3N_5 composition *via* the facile low-temperature decomposition of trichloromelamine $[(C_3N_3)(NHCl)_3]$. This inexpensive precursor rapidly and exothermically produces thermally robust carbon nitride materials. The spectroscopic (IR, NMR, X-ray photoelectron) data are consistent with an extended layered structure comprised of triazine rings and sp^2 carbon–nitrogen bonding. A comparison is made to recently proposed hydrogenated carbon nitride structural models.

Experimental procedures

Carbon nitride synthesis

The $(C_3N_3)(NHCl)_3$ precursor (trichloromelamine, Aldrich, 98%) was used as received and stored in an inert atmosphere glovebox. All solvents were reagent grade and used as received. **Safety note**: Aldrich reports that trichloromelamine does not melt until >300 °C. Since it rapidly decomposes well below this value, care should be taken when heating any potentially decomposable solid to high temperatures. The rapid decomposition of $(C_3N_3)(NHCl)_3$ was initiated in a variety of ways: *method 1* by heating the precursor (5–10 °C min^{-1}) above 185 °C in a Schlenk flask, a steel Parr autoclave, or a glass flowtube under an inert (N_2 or Ar) atmosphere; and *method 2* by rapid initiation with a resistively heated nichrome

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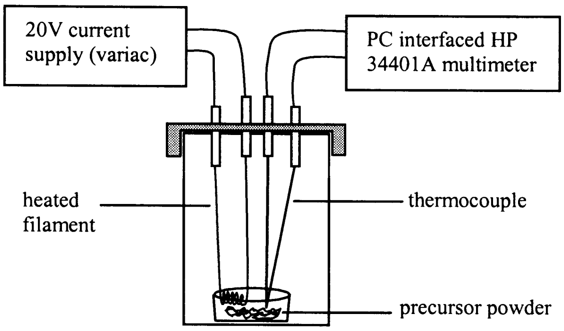

Fig. 1 Diagram of a custom-built small volume stainless steel, hot filament ignition reactor with *in situ* temperature measurement capability.

filament (*ca.* 500 °C) in a 60 ml custom calorimeter-style steel reactor (screw top, inner dimensions of 5 cm depth × 3.8 cm width, 5 ml thick walls, and a removable cap with 4 insulated posts, Fig. 1). The products were isolated within 10 minutes of the decomposition event, washed with acetone, and briefly oven dried (130 °C) in air. Typical reactions used three grams (13.1 mmol) of $(C_3N_3)(NHCl)_3$ and resulted in nearly one gram of isolated product. Chemical yields were calculated by comparison of the recovered product weight with a theoretical yield expected based on the analyzed chemical composition. The chemical yields for decompositions by method 1 (Schlenk), method 1 (Parr), and method 2 were 62%, 61%, and 61%, respectively. Annealing experiments were performed in a heated glass flow tube under argon.

Product characterization

Simultaneous thermogravimetric–differential thermal analysis experiments were performed on a Seiko Exstar 6300 system using a 5–10 °C min^{-1} ramp under flowing argon. *In situ* temperature measurements were performed with the heated filament reactor (method 2) outfitted with a 0.1 mm type K thermocouple that was placed in contact with the precursor and separated from the heated filament (Fig. 1). The thermocouple voltage changes were recorded (*ca.* 40 ms intervals) with a computer-interfaced Hewlett-Packard 34401A multimeter and converted to temperatures using HP Benchlink software. Powder X-ray diffraction was run on powders affixed to glass slides and scanned in 0.05° increments using a Siemens D5000 diffractometer. FT-IR spectra were obtained on a Nicolet Nexus 760 using KBr pellets. Solid-state ^{13}C MAS NMR was performed on a Bruker wide bore MSL 300 using a Hahn spin echo sequence, 5.75 μs 90° pulse, 200 μs delay between 90° and 180° pulses, and a 100 sec recycle delay. X-ray photoelectron spectra were obtained on powders pressed into indium foil using a PHI 5400 system with AlK_α radiation. Peak deconvolutions were made with the XPSPeak (version 4.1) program with the 100% Gaussian peak shapes (1.6–1.8 fwhm).[23] Scanning electron microscopy and energy dispersive spectroscopy were carried out on a field emission Hitachi S4000 system with a Kevex energy analyzer. Transmission electron microscopy was performed on alcohol-dispersed powders on coated Cu grids using a Hitachi H-600 STEM system operating at 100 kV. Flotation density measurements were made by suspending the sample in a $CHCl_3/CHBr_3$ or a $CH_2Cl_2/CHCl_3$ mixture. BET surface area measurements were performed on a ground sample from method 2 using a Micromeritics ASAP 2000 system. UV-visible spectra were obtained from powders suspended in ethanol solutions using an HP 8453 diode array or a Varian Cary 100 spectrophotometer. Fluorescence measurements were performed on ethanol suspensions or powders affixed to glass slides with tape using a Shimadzu RF-1501 spectrofluorophotometer with 350 nm excitation. Elemental analyses (C, H, N, Cl, O) of various samples were obtained from Desert Analytics (www.desertanalytics.com). Samples were handled and stored in air and dried at 140 °C prior to analysis. Modified CHN combustion under oxygen-free conditions was used for the oxygen determination.

Results and discussion

Carbon nitride synthesis

Trichloromelamine, $(C_3N_3)(NHCl)_3$, is an inexpensive, commercially available triazine with industrial utility as a bleaching and antibacterial agent.[24] Simultaneous thermogravimetric–differential thermal analysis (TG–DTA) of $(C_3N_3)(NHCl)_3$ shows that this involatile molecular solid rapidly decomposes in an exothermic manner beginning at 165 °C with a 66% weight loss (Fig. 2a). The solid remaining after this energetic decomposition is stable until nearly 600 °C. The observed TGA weight loss is close to a 60% value calculated for the removal of three HCl and one N_2 from $(C_3N_3)(NHCl)_3$ to produce a solid with a C_3N_4 composition. An ideal trichloromelamine decomposition is shown in eqn. (1).

$$(C_3N_3)(NHCl)_3 \rightarrow C_3N_{4+x} + 3\ HCl + (2 - x)/2\ N_2 \quad (1)$$

Intrigued by the TGA result, we explored the large-scale, thermally induced decomposition of trichloromelamine *via* heating ($T \geqslant 185$ °C) in a Schlenk flask or Parr reactor [method 1] and by initiation with a heated filament [method 2]. The exhaust gas from the Parr decomposition showed distinct HCl signatures by gas phase IR and precipitated AgCl from a silver nitrate solution. A base titration of the gaseous effluent was consistent with over 80% of chlorine present in gaseous acidic form. An *in situ* reaction temperature measurement demonstrated that

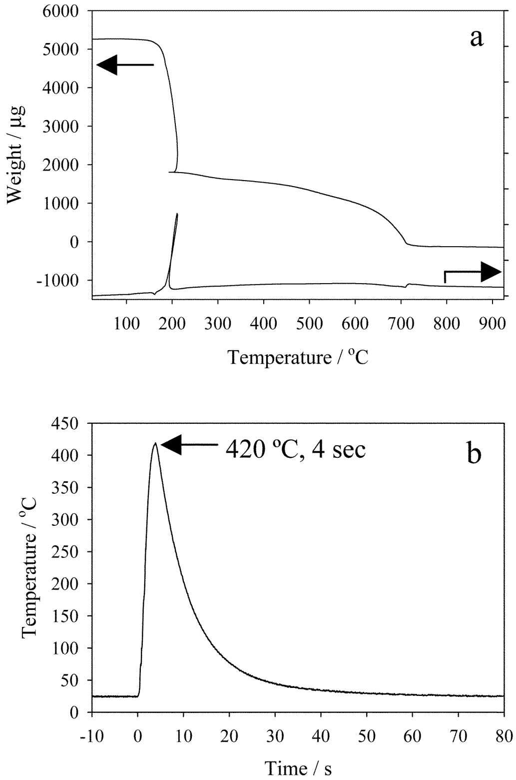

Fig. 2 (a) Thermogravimetric–differential thermal analysis of $(C_3N_3)(NHCl)_3$ heated under an argon flow. The TGA discontinuity near 200 °C is an artifact due to rapid heat evolution from the decomposing sample. (b) An *in situ* temperature profile of the heated filament initiated decomposition of $(C_3N_3)(NHCl)_3$. The decomposition is initiated at $t = 0$ s.

Table 1 Compositional data on various carbon nitrides

Product	C wt%	N wt%	H wt%	Cl wt%	O wt%	Formula
Method 1 (Schlenk)	32.08	59.93	1.94	0.47	4.00	$(\mathbf{C_3N_{4.81}})H_{2.16}Cl_{0.01}O_{0.28}$
Method 1 (Parr)	34.21	60.01	1.56	0.60	1.78	$(\mathbf{C_3N_{4.51}})H_{1.63}Cl_{0.02}O_{0.12}$
Method 2 (filament)	34.17	61.94	1.83	0.16	1.35	$(\mathbf{C_3N_{4.66}})H_{1.91}Cl_{<0.01}O_{0.09}$
Method 1 + 400 °C ann.[a]	34.50	60.87	1.96	0.25	2.76	$(\mathbf{C_3N_{4.54}})H_{2.03}Cl_{0.01}O_{0.18}$
Method 1 + 510 °C ann.[b]	34.27	57.65	1.02	0.25	7.34	$(\mathbf{C_3N_{4.33}})H_{1.06}Cl_{0.01}O_{0.48}$
Method 1 (Parr) + NH_4OH	35.29	62.19	1.66	0.25	0.89	$(\mathbf{C_3N_{4.53}})H_{1.68}Cl_{<0.01}O_{0.06}$

[a] Flowtube decomposition followed by 15 h anneal. [b] Further annealing of previous sample for 15 h.

the exothermic $(C_3N_3)(NHCl)_3$ decomposition reaches temperatures above 400 °C within seconds and rapidly cools to room temperature (Fig. 2b).

Bulk chemical analyses of the isolated tan to light orange solid products verify that they have high nitrogen contents, namely C_3N_{4+x} where $0.5 < x < 0.8$, and have lost nearly all chlorine (see Table 1). There is consistency in product compositions and yields ($>60\%$) for both decomposition methods, which result in materials with some of the highest nitrogen to carbon ratios reported to date ($N/C > 1.5$). The residual hydrogen incorporation may be due to –NH groups or a minor ($<2\%$) melamine $[(C_3N_3)(NH_2)_3]$ impurity that is present in the precursor. The oxygen content is low, especially considering that these materials are worked up with acetone and handled in air.

Structural characterization

Powder X-ray diffraction (XRD) of these C_3N_{4+x} materials revealed only one distinct broad peak (fwhm ≈ 1.2°) at 27.5° (3.24 Å), suggesting that the major structural ordering is related to a graphite-like π stacking of triazine ring layers.[16,18,21,22] Due to disorder in these carbon nitride materials, a variety of spectroscopic tools were utilized to gain structural insight. The IR characteristics of the C_3N_{4+x} samples are compared to the $(C_3N_3)(NHCl)_3$ precursor in Fig. 3. The major absorptions occur in the 900–1700 cm^{-1} region, consistent with significant carbon/nitrogen single and double bond character. Increased absorption in the 1000–1300 cm^{-1} region for C_3N_{4+x} relative to the precursor indicates an increase in C–C and/or C–N single bond character. Absorptions between 1280–1380 cm^{-1} have been ascribed to secondary (NC_2) and tertiary (NC_3) amine fragments.[22] The absorption near 800 cm^{-1} is a triazine ring mode, suggesting that the (C_3N_3) motif is retained in the C_3N_{4+x} product. There is little absorbance at 2170 cm^{-1} confirming that only very minor C≡N or N=C=N components are generated during the trichloromelamine decomposition. Absorbance in the 3200 cm^{-1} region is related to residual N–H components. Overall, the major IR signatures are consistent with the general characteristics other carbon nitride powders with greater than 50 at% nitrogen.[16–19,21,22] The materials produced in the present study may be most closely related to previous triazine polymers ($C_6N_9H_4Cl$),[21] which after loss of an HCl group would have a $C_3N_{4.5}H_{1.5}$ formula, similar to those reported here. The IR of a more condensed triazine $C_3N_{4.3}H_{1.0}$ network[22] and that of ref. 21 have many similar features to the IR data in Fig. 3.

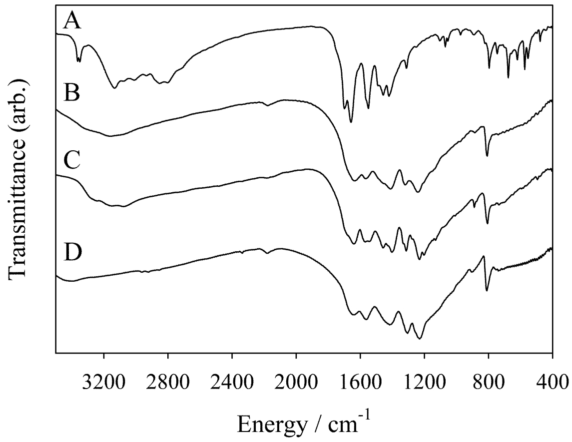

Fig. 3 Infrared spectroscopic comparison between the $(C_3N_3)(NHCl)_3$ precursor (A), the C_3N_{4+x} decomposition products from method 2 (rapid filament initiation) (B), products from method 1 (Parr reactor heating) (C), and a sample from method 1 annealed at 510 °C (D).

The solid-state ^{13}C MAS NMR spectrum of C_3N_{4+x} has a broad peak centered at 156 ppm with a small shoulder at 163 ppm. This region is characteristic of sp^2-bonded carbon in a deshielded environment consistent with a high number of directly bonded nitrogen neighbors, *e.g.* carbon in a triazine-like or graphitic (sp^2) environment.[18c,19,21,25] The absence of any other carbon signals indicates that these amorphous C_3N_{4+x} networks retain local structure and bonding reminiscent of the triazine ring motif. For comparison, molecular triazines, such as $(C_3N_3)(X)_3$, where X = Cl or N_3, have carbon resonances near 170 ppm and theoretical studies on graphitic sp^2 C_3N_4 predict a ^{13}C resonance near 150 ppm.[26]

X-Ray photoelectron spectroscopy (XPS) is sensitive to light element chemical environments and has shown some utility in investigating carbon nitride structural environments. The XPS carbon and nitrogen core level (1s) spectra for carbon nitrides from method 1 and 2 are compared in Fig. 4. Atmospheric exposure and the acetone wash likely result in some surface oxygen components and the carbon peak(s) centered around 288–290 eV is consistent with carbonate or carbonyl-like species.[27] The nitrogen spectra also have a shoulder between 401–402 eV that may correspond to N–O surface species. Survey mode spectra show that oxygen signals have no energy

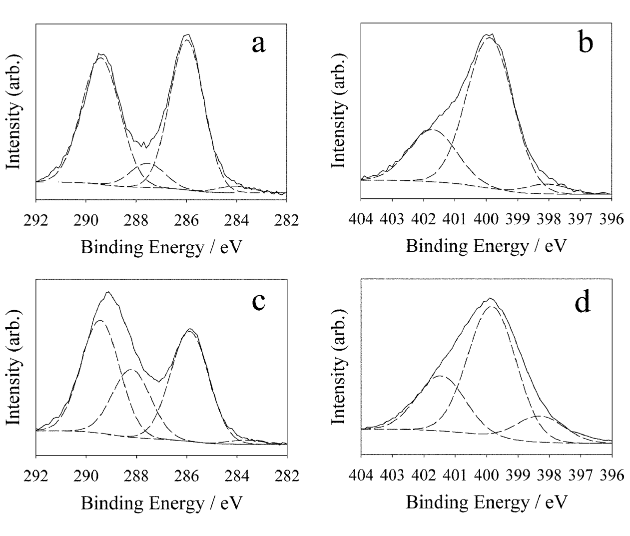

Fig. 4 X-Ray photoelectron spectroscopy data with peak deconvolutions (dashed lines) for the carbon 1s (a, c) and nitrogen 1s (b, d) binding energy distributions of C_3N_{4+x} materials from method 1 (a, b) and method 2 (c, d). Simulated peaks for each graph are centered at (eV): (a) 289.4, 287.6, 286.0, 284.1, (b) 401.7, 399.9, 398.1, (c) 289.4, 288.2, 285.9, 283.4, and (d) 401.4, 399.8, 398.3.

dependent intensity loss, indicating that oxygen originates primarily from surface species. Argon ion sputtering was not used to clean the powder surface because numerous studies have shown that this high energy process results in preferential nitrogen loss and changes in nitrogen chemical environment. Unsputtered samples had approximate XPS nitrogen compositions in the 40–50 at% range. The most relevant C–N XPS bonding peaks are found at 284–288 eV for carbon and 398–401 eV for nitrogen. The major carbon peak is near 286 eV and is consistent with carbon in a nitrogen-rich environment.[28] In addition there is a small peak near 284 eV that may correspond to C–H species. The nitrogen peak at 400 eV has been attributed to nitrogen in a substitutional graphite (sp^2) structure.[28,29] The nitrogen shoulder at 398 eV may correspond to nitrogen connected to sp^3 hybridized carbons, to two-coordinate (NC_2) structures, or to species with N–H character.[28–30] The latter two choices seem most likely in the present study.

Microstructural analysis

The rapidly formed sp^2 bonded carbon nitrides have densities greater than conventional organic polymers such as polyethylene or polystyrene (0.9–1.2 g cm^{-3}) but less dense than graphite (2.3 g cm^{-3}). The flotation density for carbon nitride from method 1 (Parr) was 1.7 g cm^{-3}, while the method 1 (Schlenk) and method 2 products were less dense at 1.4 g cm^{-3}. The apparent density difference may be related to additional compaction during Parr synthesis since the gaseous byproducts remain in the reactor and generate 20–30 atm (2–3 MPa) of pressure during the synthesis. The bulk surface area of C_3N_{4+x} by method 2 is 5 m^2 g^{-1}, consistent with a moderately porous structure. Scanning electron microscopy (SEM) shows that the C_3N_{4+x} materials formed by either decomposition method have a glassy microstructure with large holes and voids (Fig. 5 top). On higher magnification a fused spherical particle morphology is evident on the solid's surface (Fig. 5 middle). The spherical particles range from roughly 100 to 300 nm in diameter. Transmission electron microscopy (TEM) clearly shows the fused nanosphere structure, however no distinct internal sphere structure or crystallinity by electron diffraction was detected (Fig. 5 bottom). By TEM, larger plate-like fragments were also observed that appeared to be comprised of fused spherical particles. The random pore morphology displayed in the current systems is qualitatively similar to those observed in our previous work with $(C_3N_3)(N_3)_3$ decomposition,[19] however the macropore dimensions observed here are about 100 times larger (Fig. 5 top). In the azide case, pores were generated *via* N_2 gas evolution from a precursor melt, in contrast to the current study where rapid trichloromelamine decomposition occurs without melting, possibly with some gas phase condensation that could help generate spherical morphologies.

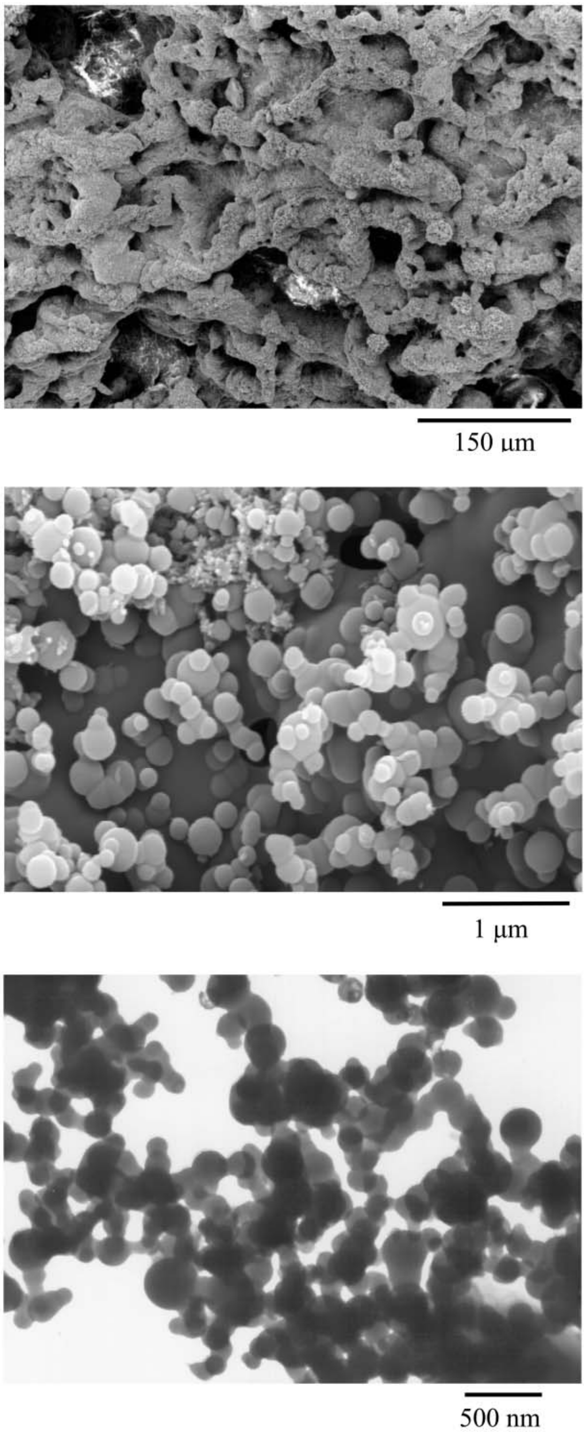

Fig. 5 Scanning electron (top and middle) and transmission electron (bottom) micrographs of C_3N_{4+x} produced *via* the rapid decomposition of $(C_3N_3)(NHCl)_3$.

Optical properties

Several photoluminescent species based on molecular triazines,[31] trigonally planar triarylamines,[32] and amorphous carbon nitride films[33] have been reported and some of them exhibit emission in the blue region. Carbon–nitrogen heterocyclic molecules and triamino systems have also been used as electron and hole transporting layers in light emitting systems.[34] In addition, luminescent organic polymers are known.[35] The UV-vis absorption properties of C_3N_{4+x} are consistent with a conjugated ring system with UV-vis absorption features at 270 (weak shoulder), 325, and 375 nm (Fig. 6a). These absorptions are in the range observed for molecular nitrogen-containing aromatic systems where the N (lone pair) to π* transitions are dominant. The carbon nitride powders, particularly those from method 1 (Parr), also exhibit blue luminescence when suspended in solution or affixed to a glass support (Fig. 6b). Due to low concentrations present in alcohol suspensions, the intensity is significantly lower than observed in the solid state. The luminescence from method 1 (Parr) powders is visibly observed as a yellow-green glow under illumination with a handheld UV lamp. Note that C_3N_{4+x} photoluminescence is still observed after annealing to 400 °C, in contrast to carbon nitride film studies where luminescence vanishes after annealing at 200 °C.[36]

Thermal and chemical stability

During the exothermic synthesis, the carbon nitride product is briefly subjected to temperatures above 400 °C. TG–DTA

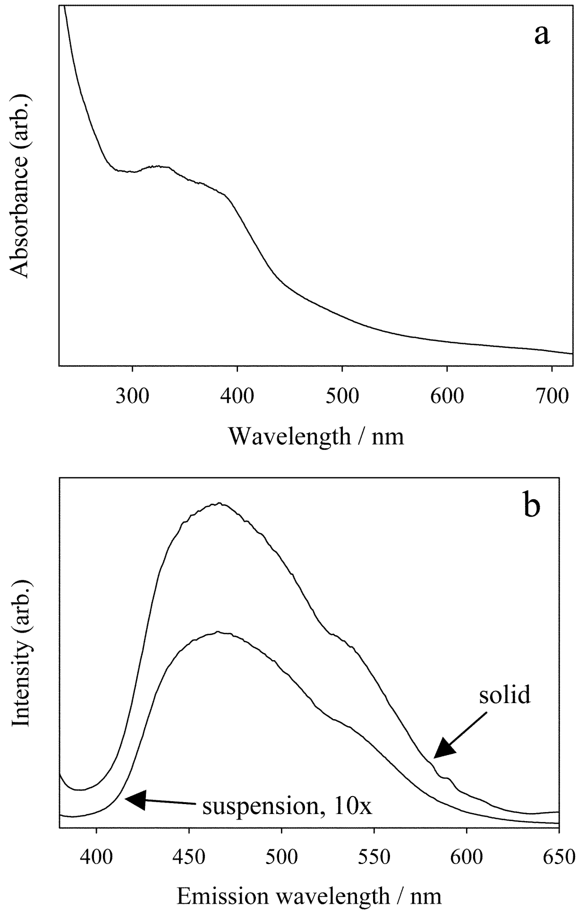

Fig. 6 UV-vis (ethanol suspension) spectrum (a) and photoluminescence (ethanol suspension and solid) measurements (b) on C_3N_{4+x} powder synthesized by method 1.

analysis of the isolated carbon nitride shows minor weight loss between 500–600 °C (~ 15%) and complete evaporation and/or decomposition by 750 °C, leaving no solid residue (Fig. 7). Note that the thermal stability of isolated C_3N_{4+x} mirrors that of the residue in the precursor TG–DTA shown in Fig. 2a. The carbon nitride material after annealing up to 510 °C has similar IR spectra to the starting powder (Fig. 3d), however the nitrogen and hydrogen contents are slightly lower (Table 1). At temperatures above 550 °C, the sample begins to evaporate or decompose and completely volatilizes by 640 °C.

The carbon nitride powders are somewhat hydrophobic and are insoluble in common solvents including water, alcohols, DMF, NMP, THF, diethyl ether, pentane, and toluene. An acetone-washed 30 mg C_3N_{4+x} sample from method 1 (Parr) acidified a 3 ml sample of deionized 18 MΩ water (pH: 7 to 3). This acidification would require 3 μmol H^+, which is coincidentally nearly equal to the residual chloride content of our materials. This suggests that the as-synthesized solids may be acid-doped with protonated nitrogen sites and chloride counter ions. When C_3N_{4+x} was placed in 14.7 M NH_4OH no apparent reaction or significant change in composition occurred (see Table 1), suggesting that the above change in acidity is not a result of hydroxide abstraction from water. The carbon nitride also appears stable in 12 M HCl, however it changes from an orange to light yellow color and disperses more readily in solution. The IR spectra of base-treated carbon nitride samples are essentially unchanged from those shown in Fig. 3, however acid exposed samples show a decrease in intensity in the 2200 cm^{-1} and 1250–1350 cm^{-1} regions.

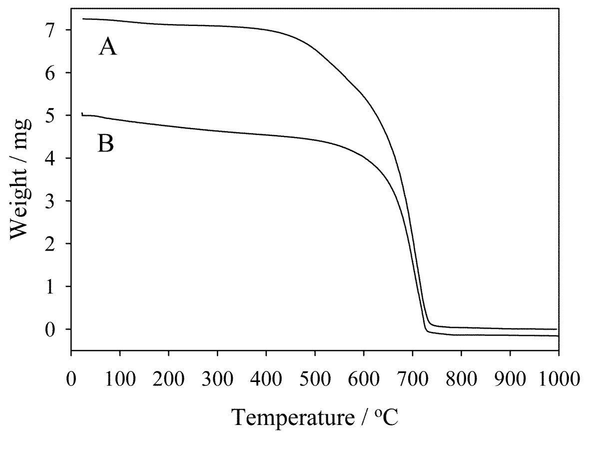

Fig. 7 Thermogravimetric–differential thermal analysis of C_3N_{4+x} from method 2 (A) and method 1 (B) and heated under flowing argon.

Structural possibilities

Trichloromelamine may decompose and produce a variety of triazine ring linkage units (Fig. 8, fragments 1–5). Ordered planar C_3N_4 structures have been proposed as regularly substituted derivatives of graphite (Fig. 8, Layer A).[3a] This system is a graphite-like structure with triazine rings bridged by trigonally planar nitrogens (Fig. 8, fragment 1). A C_3N_{4+x} compound with $x > 0$ could be derived by adding fragments 2–5 to Layer A. Some of these fragments will also introduce hydrogen content. The loss of amine groups could also leave a hydrogen-terminated triazine (6).

On the basis of crystallographic data, two hydrogenated carbon nitride layered structures were recently proposed that are related to Layer A with an ordered removal of C_3N_3 rings and hydrogenation of the nitrogens that were bonded to the missing rings. The remaining triazine rings are either connected by 2 N–H and one trigonal planar N bond (Layer B)[22] or 3 N–H bonds (Layer C).[21] From bulk compositions and structural analyses, trichloromelamine likely decomposes to a disordered structure related to Layer C ($C_3N_{4.5}H_{1.5}$). The lack of crystalline order in the *ab*-plane of our materials suggests that some triazines are not linked in an ordered fashion. This could be accomplished by replacing some fragment 5 species in Layer C with fragments 4 and 6. Upon annealing these weaker links may preferentially decompose and rearrange to a Layer B-like structure ($C_3N_{4.3}H_{1.0}$). In our amorphous systems, the hydrogen residues may also be concentrated on particle surfaces or at layer edges to passivate strained or dangling bonds.

Ideally each nitrogen in any of the theoretical sp^2 C_3N_4 conjugated networks described above will have a lone pair that could serve as a Lewis base coordination site on the surface or the interior of the solid carbon nitride. Previous studies have observed some transition metal uptake after synthesis.[22] We are currently exploring the possibility of incorporating metal halides (*e.g.* $NiCl_2$ and $CoCl_2$) during C_3N_{4+x} synthesis using method 2. Initial indications are that after reaction and a water workup, metal is retained in the carbon nitride structure. Details on this work and further carbon nitride structural and chemical reactivity studies will be reported elsewhere.

Conclusions

This article describes an extremely rapid and straightforward method to produce gram quantities of a high-nitrogen content carbon nitride from a single molecular precursor, $(C_3N_3)(NHCl)_3$. This precursor exothermically decomposes, briefly generates internal temperatures near 400 °C, and results in an amorphous C_3N_{4+x} material with one of the highest N/C ratios (> 1.5) reported to date. Spectroscopic analysis of this carbon nitride is consistent with a layered structure containing significant triazine and sp^2 bonding character. The as-synthesized products are thermally robust up to 600 °C, have a moderately

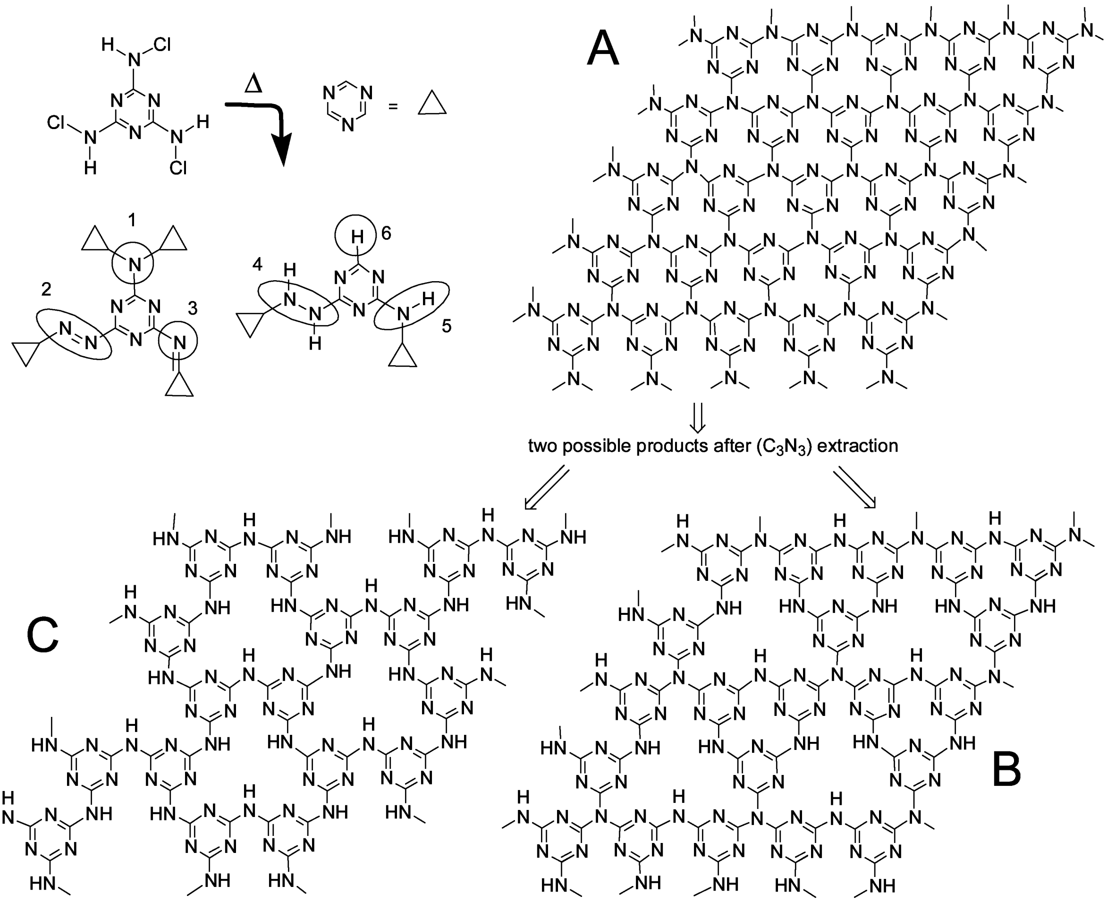

Fig. 8 Possible triazine fragments (1–6) resulting from $(C_3N_3)(NHCl)_3$ decomposition and comparison of structural models (A–C) proposed for layered C_3N_4 materials.

porous structure with nanospherical morphologies, and show evidence of blue photoluminescence.

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