



Graphitic carbon nitride materials synthesized via reactive pyrolysis routes and their properties[☆]

Jian Zhang, Yingai Li, Pinwen Zhu^{*}, Dahai Huang, Si Wu, Qiliang Cui, Guangtian Zou

State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, PR China

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ABSTRACT

The present article describes the large-scale powder syntheses of high nitrogen-content graphitic carbon nitride materials with unique belt-like or tubular morphologies via reactive pyrolysis of two molecular precursors, melamine and cyanuric chloride. The structural characterizations based on XRD indicate the presence of turbostratic ordering in the graphene layers of carbon nitride. Spectroscopic analyses via FTIR technique are consistent with the layered structure with sp^2 -hybridized bonding features. Morphological investigations via SEM and TEM reveal the elaboration of micron-sized tubular hollow vessels. The optical properties of the prepared samples are investigated via UV absorption and PL spectroscopy, which exhibit the semiconductor-like absorption edge at 2.7 to 2.8 eV and a well-defined PL emission band at 425 nm.

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1. Introduction

Over the last two decades, considerable research efforts have been devoted to the synthesis of carbon nitrides for their promise as high-performance materials with hard, lightweight, and thermally stable properties [1–4]. In particular, graphitic carbon nitride has attracted much attention due primarily to its potential applications as the precursors of the postulated dense superhard 3D carbon nitride polymorphs [5] and novel nanostructured materials [6]. Meanwhile, it has also been reported that graphitic carbon nitrides may be used as catalytic supports, lubricants, optical, and electronic materials, as well as in drug delivery and gas storage [7].

In most of the postulated structures of graphitic carbon nitride, *s*-triazine ring (C_3N_3) systems are cross-linked by N atoms [2,8,9] or carbodiimide groups [10] as building blocks to form extended 2D sheets. Another possible building block that is usually adopted to construct the graphene-like C_3N_4 sheets is tri-*s*-triazine or heptazine ring (C_6N_7), which is cross-linked by N atoms or nitrogenous groups in similar ways [11–13]. DFT calculations have shown that graphitic C_3N_4 based on tri-*s*-triazine ring systems should be more stable in energy than those containing *s*-triazine rings [13]. This theoretical assumption may be supported by the fact that melem (triamino-tri-*s*-triazine) readily forms during thermal condensation of melamine, which might be an experimental indication that graphite-like C–N materials as well as graphitic carbon nitride itself

presumably contain tri-*s*-triazine instead of *s*-triazine rings [14]. Considerable progress in the preparation, structure determination, and properties investigation of the triazine and/or heptazine ring containing systems has been made recently.

Numerous attempts to prepare graphitic carbon nitride via the thermal condensation of melamine as well as its derivatives have been performed [3]. Yet all attempts have been invariably spoiled by the presence of impurities, or otherwise by the amorphous nature of the obtained samples. However, the controlled pyrolysis of CN_xH_y precursors remains to be a most promising synthetic strategy to obtain reasonably well-defined carbon nitride materials [15,16]. In order to fulfill the quest for the contamination-free prototype carbon nitride materials, we present in this work large-scale synthesis of nitrogen-rich graphitic carbon nitrides via reactive pyrolysis of melamine and cyanuric chloride.

2. Experimental

As raw materials, cyanuric chloride ($C_3N_3Cl_3$) and melamine ($C_3N_6H_6$) were obtained commercially and used without further purification. Fine powders of cyanuric chloride and melamine were mixed with a molar ratio of 1:2, serving as the precursors. The mixed powders were subjected to ball milling until a homogenous mixture was obtained and then shaped into cylindrical columns hefting about 3 g each.

Two synthetic routes were employed to investigate the reactive pyrolysis processes of the precursors. In the first route, the precursor columns were placed in stainless steel autoclaves with a 30 ml capacity. The manipulations were carried out in a nitrogen-filled glove box to prevent the reaction system from being contaminated by moisture and oxygen. The autoclaves were heated at 400, 500, and

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^{*} Corresponding author. Tel./fax: +86 431 85168881.

E-mail address: zhupw@jlu.edu.cn (P. Zhu).

600 °C, respectively, for typically 6 hours. Then the autoclaves were cooled to ambient temperature naturally and the products were collected.

In the second route, the precursor column was placed in a quartz tube, 25 mm in inner diameter and 1200 mm in length. Firstly, the quartz tube was evacuated (<1 Pa) by a pump and heated to 150 °C in an electric furnace. Such condition was maintained for about 24 hours to eliminate the adsorbed moisture and oxygen. Then the quartz tube was heated to 800 °C and maintained for 6 hours. The quartz tube was cooled to ambient temperature naturally and floccular powders with yellow to brown colors were collected from the inner wall of the quartz tube where the temperature ranged from about 400 to 600 °C during the pyrolysis. No product could be found at the central high temperature region.

In both routes, the collected powders were washed with acetone, ethanol, and distilled water repeatedly to remove the residual reactants and the byproducts and then dried in a hot air flow. The samples obtained in the first route were labeled AC400, AC500, and AC600, respectively, corresponding to the pyrolysis temperatures. The sample obtained in the second route was labeled QT800.

Structural analysis of the samples was carried out by powder X-ray diffraction (XRD) on a Rigaku D/max γ A diffractometer working with Cu $K\alpha$ radiation ($\lambda = 0.154178$ nm). The Fourier transform infrared (FTIR) spectroscopy studies were carried out on a Nicolet Avatar 360 FTIR spectrometer with the sample powders diluted in KBr pellets. The scanning electron microscopy (SEM) images of the sample were taken on a HITACHI S4800 microscope working at 20.0 kV, which is equipped with an energy dispersive spectrometer (EDS). The transmission electron microscopy (TEM) images of the samples were obtained via a H8100 transmission electron microscope using an accelerating voltage of 200 kV. The ultraviolet–visible (UV–Vis) absorption spectra of the samples were taken on a Shimadzu UV-3150 spectrometer and the photoluminescence (PL) measurements were conducted under 360 nm UV fluorescent light excitation by a Shimadzu RF-5301PC spectrophotometer.

3. Results and discussion

It has been reported that the pyrolysis of melamine, as well as cyanamide, dicyandiamide and ammonium dicyanamide, at a temperature about 450 °C leads to the formation of melem [14]. Whereas the thermal polycondensation of ADCT (2-amino-4,6-dichloro-*s*-triazine) at a temperature of 500 °C has been found to yield an amorphous carbon nitride material [17]. It may be inferred that 500 °C should be a critical temperature for the formation of condensed heptazine nuclei from a starting material containing triazine rings through thermal condensation routes. Below 500 °C, molecular solids such as melem may be formed. Above 500 °C, high degrees of polymerization will occur, resulting in the formation of extended CN networks with layered character. This hypothesis may be confirmed by our experimental

results. The postulated chemical reactions of the precursors under different pyrolysis temperatures are schematically illustrated in Fig. 1. The overall yields of products may be roughly estimated to be 93% for AC400, 87% for AC500, 85% for AC600, and 80% for QT800.

The typical XRD patterns of the samples are shown in Fig. 2. A series of diffraction peaks may be discerned for sample AC400 in the 2θ range between 10° and 35°. In fact, the XRD pattern illustrated in Fig. 2(a) resembles to a large extent that of the crystalline powders of melem, which has been indexed with a monoclinic unit cell [14]. Thus it can be implied that the reactive pyrolysis of melamine and cyanuric chloride at 400 °C in a N_2 filled autoclave may yield a melem-like molecular solid. However, the situations are quite different when the pyrolysis temperatures are raised. As for AC500, only a strong sharp peak at the position of $2\theta = 27.86^\circ$ and a dispersive weak band at the position of $2\theta = 57.61^\circ$ could be observed in the pattern, with the corresponding d -spacings to be 0.320 and 0.160 nm, which are in good agreement with those of the (0 0 2) and (0 0 4) lattice planes of graphitic carbon nitride [18,19]. The absence of other reflections implies that the crystallization is still not good enough. It may be speculated that there may be regular stacking of the graphene-like CN monolayers along the $\langle 0\ 0\ 2 \rangle$ direction, while some degree of disorder may exist in the a – b dimensions. AC600 exhibits similar XRD characteristics as AC500. However, the corresponding diffractions have relatively narrower FWHM (full width at half maximum) and shift towards low-angle direction, indicating a higher degree of crystallinity with the increasing of pyrolysis temperature. In the case of QT800, it can be seen that the diffraction peak corresponding to the (0 0 2) lattice planes of graphitic carbon nitride is remarkably widened and the (0 0 4) diffraction is hardly discernable, implying the crystallinity is much lower. This is reasonable since QT800 is produced via a vapor phase transfer process under vacuum, in which the quenching effects may play a part in the crystallization.

The typical FTIR spectra of the prepared samples are displayed in Fig. 3. As for AC400, a broad but structured absorption band in the region between 800 and 1850 cm^{-1} dominates the spectrum, with distinguishable maxima at 810, 890, 1239, 1325, 1400, 1461, 1555, and 1634 cm^{-1} , and shoulders at about 875, 1010, 1082, 1130, 1207, 1537, 1574, and 1683 cm^{-1} . The well-resolved bands may indicate a fairly high degree of ordering, which is in accordance with our XRD investigations. Owing to obvious analogies with the vibrational spectra of heptazine compounds already present in the literature, such as those of $C_6N_7Cl_3$, $C_6N_7(NH_2)_3$, and $C_6N_7(NH_2)_3$ [13,14,17,20,21], the observed absorptions may be readily assigned to the skeletal vibration modes belonging to the C_6N_7 nucleus. The detailed results of the assignments are listed in Table 1. However, it should be noted that the selection rules seem to be broken, since some modes that is only Raman-active (and IR inactive) can also be observed in the IR spectra. It is reasonable in the sense that the local symmetry of the C_6N_7 nucleus may be altered during the polycondensation process. As for AC500 and AC600, the FTIR spectra exhibit signals at similar wavenumbers as that

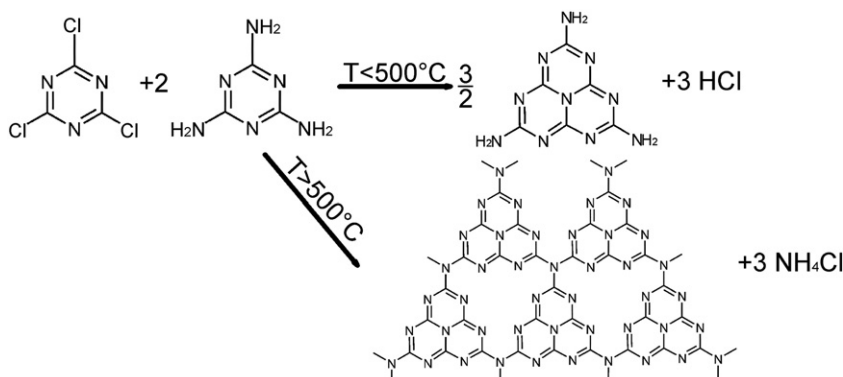


Fig. 1. The postulated chemical reactions of the precursors under different pyrolysis temperatures.

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