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Ionothermal Synthesis of Crystalline, Condensed, Graphitic Carbon Nitride

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Abstract: Herein we report the synthesis of a crystalline graphitic carbon nitride, or g-C_3N_4, obtained from the temperature-induced condensation of dicyandiamide ($NH_2C(=NH)NHCN$) by using a salt melt of lithium chloride and potassium chloride as the solvent. The proposed crystal structure of this g-C_3N_4 species is based on sheets of hexagonally arranged s-heptazine (C_6N_7) units that are held together by covalent bonds between C and N atoms which are stacked in a graphitic, staggered fashion, as corroborated by powder X-ray diffractometry and high-resolution transmission electron microscopy.

Keywords: carbon nitrides · covalent frameworks · layered compounds · salt melt · solid-state structures

Introduction

Carbon nitride materials are regarded as a valuable extension of carbon in material applications and have experienced a renaissance of activity in recent years. However, synthetic attempts that used chemical or physical vapour deposition techniques mostly yielded a variety of non-stoichiometric, amorphous solids.[1,2] At ambient conditions, graphitic C_3N_4 (g-C_3N_4) is regarded as the most stable allotrope, and there are a large number of reports in the literature that approach the synthesis of different modifications of this material.[3] Several C/N/H/S-containing compounds that were considered to be promising precursors for chemical and bulk routes towards pure CN_x phases, such as s-triazines (in particular their chlorides and fluorides),[4–6] *s*-heptazines[7–9] and thiocyanates, have been identified.[10,11] Bulk synthesis routes based on these precursors have not so far yielded the desired highly condensed, crystalline C_3N_4 phases, but rather give incompletely condensed materials. Elemental microanalyses of those substances show hydrogen contents of up to 2 wt%, which resembles a stoichiometry closer to that of melon (poly[(8-amino-1,3,4,6,7,8,9,9b-heptaazaphenalen-2,5-diyl)imine]; 1.5 wt% hydrogen).[12] Representative examples of the many attempts to synthesise C_3N_4 structures by high-pressure, high-temperature (HP-HT) routes are slow thermal decomposition[13] and detonative synthesis[14] of triazido-*s*-triazine, $C_3N_3(N_3)_3$, which gave a series of amorphous C/N/H/O-containing compounds, that is, carbon nanotubes in the former route and nanoparticles in the latter. It should be noted that the field of HP-HT synthesis was advanced very recently by Riedel, Kroke, McMillan et al., who showed that conversion of dicyandiamide under HP-HT conditions indeed gives a crystalline carbon nitride imide phase, $C_2N_2(NH)$.[15] A more complete discussion of the history of both chemical and physical approaches to a multitude of CN_x phases can be found elsewhere.[3,16]

In analogy to the graphite/diamond system, a graphitic (sp^2 hybridised) form of carbon(IV) nitride (g-C_3N_4) could be transformed into the sp^3 hybridised form via high-pressure techniques.[17] Furthermore, g-C_3N_4 is a thermally stable catalyst[18–20] and its uses for gas storage are discussed.[21]

Kroke et al. proposed that g-C_3N_4 consists of sheets of highly ordered tri-*s*-triazine moieties connected through planarised tertiary amino groups, as depicted in Scheme 1.[3] The tri-*s*-triazine-based structure was postulated on the basis of density functional theory calculations to be more stable at ambient conditions.[22] The underlying thermal self-condensation mechanism of cyanamide that leads to these structures was investigated by Schnick et al.[23] It is based on the molecular reaction of cyanamide and its successive con-

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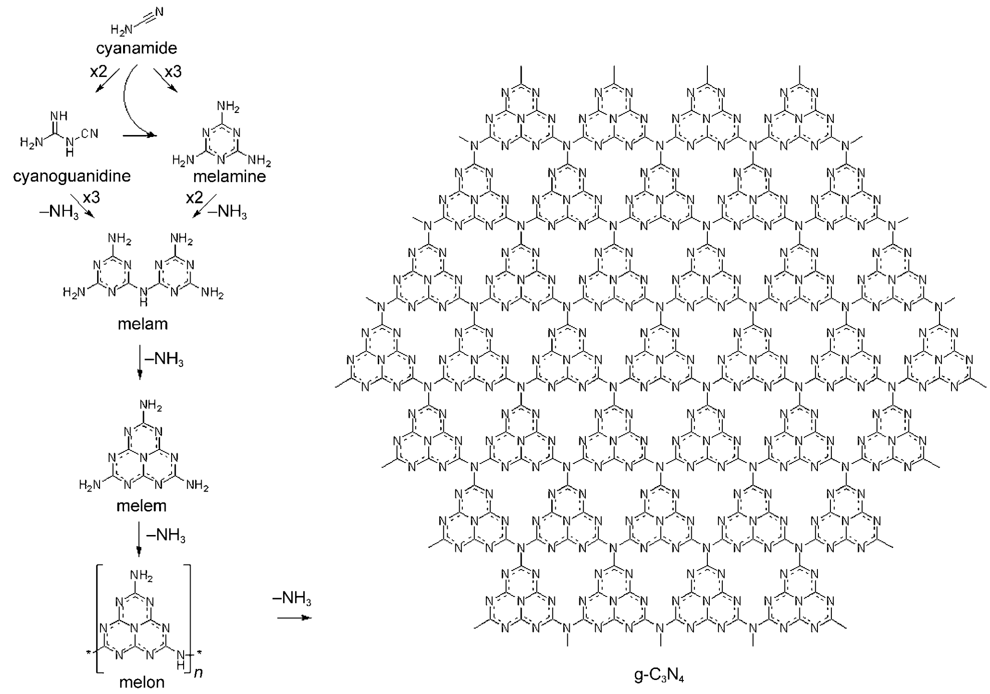

Scheme 1. Condensation reactions of cyanamide that give discrete oligomers, polymers and extended networks.

densation products, which is driven by both deamination and the formation of aromatic units (Scheme 1).

Incomplete condensation or polymerisation in the bulk, is widely acknowledged as being a predominantly kinetic problem. Schnick et al. showed that the bulk reaction most likely does not proceed significantly past the polymeric form (melon; Scheme 1).[23] We claim that this problem can be overcome by using an appropriate solvent. However, the nature of the polycondensation reaction of *s*-heptazine derivatives, namely, the thermally induced reaction at temperatures of 400 °C and above, discards all standard solvents. Kanatzidis et al. have previously pointed out the limited choice of appropriate media for synthetic applications at intermediate temperatures (i.e., 150–350 °C), and have successfully applied alkali metal polysulfide melts in the synthesis of low-dimensional ternary chalcogenides.[24] The eutectic mixture of lithium chloride and potassium chloride (45:55 wt %, $T_m = 352$ °C)[25] has been known for some time as a medium for electrochemical processes, in particular in high-temperature galvanic cells[26] and more recently as a solvent for salts of lanthanides and actinides.[27] In the 1960s, Sundermeyer et al. showed that known organic chemistry can be performed in molten salts.[28,29] Among the successfully synthesised compounds were carbonyl and fluorocarbonyl pseudohalogenides[30] and cyanides, cyanates and thiocyanates of both silicon and carbon.[31] In this context, Sundermeyer et al. explicitly point out the good solvating properties of the eutectic mixture of LiCl and KCl with respect to nitrides, carbides, cyanides, cyanates and thiocyanates.

For our means, the LiCl–KCl eutectic mixture was identified as a good solvent owing to its high-temperature stability, non-corrosive properties and its melting point below the polycondensation point of *s*-heptazine. Furthermore, good solvation of the small molecular precursors and subsequent aggregates of higher molecular weight facilitated the condensation of the carbon nitride network. Following the lead from other groups who have shown that crystalline C/N phases are indeed obtainable, we hope to provide proof that the synthesis of an extended, highly crystalline, graphitic carbon nitride is possible.

Results and Discussion

The composition of a sample of g-C_3N_4, according to a preliminary elemental microanalysis, was as follows: 31.9 % C, 52.7 % N, 0.67 % H and 4.9 % O, the difference from 100 wt % is presumably due to chelated salt. Treatment of this sample with boiling sulphuric acid and subsequent Cl-, Li- and K-titration gave 3.30 % Cl, 2.62 % Li and 0.24 % K. Note that the hydrogen content of any C_3N_4-like material prepared from thermally induced bulk condensation without molten salt as a solvent gave no value better than 1.5 wt %, which would correspond to the hydrogen content of melon rather than to an extended C_3N_4 sheet. Note also that a major part of the hydrogen content can be attributed to adsorbed water. A reasonable formulation of the dried C_3N_4 material was found to be $C_{3.0}N_{4.2}H_{0.07}$, which corresponds to the expected formula of an extensively condensed material with a low degree of defects and few terminal amino groups. Strikingly, the Cl-, Li- and K-titration revealed an excessive amount of lithium that was too large to be attributed to residual salt and too small to be a periodically incorporated constituent of the carbon nitride framework. The elusive nature of lithium with respect to most crystallographic and analytical methods is a challenge to all general statements about its role and situation in the material at hand, and will be the subject of future investigations.

The vibrational spectra of dicyandiamide condensed in molten salt and in the bulk were compared with the spectrum of melem (Figure 1). Several strong bands in the 1200 to 1600 cm^{-1} region were found, which correspond to the typical stretching modes of CN heterocycles. Additionally, the characteristic breathing mode of the triazine units at 800 cm^{-1} was observed. It should be noted that the broad bands at around 3000 cm^{-1} that are indicative of secondary and primary amines (and their intermolecular hydrogen bonding) are absent in the spectrum of the condensation product prepared in molten salt. Put in context with the low hydrogen content, this find indicates a more thorough condensation of the C_3N_4 material in the molten salt than any bulk condensation could so far allow.

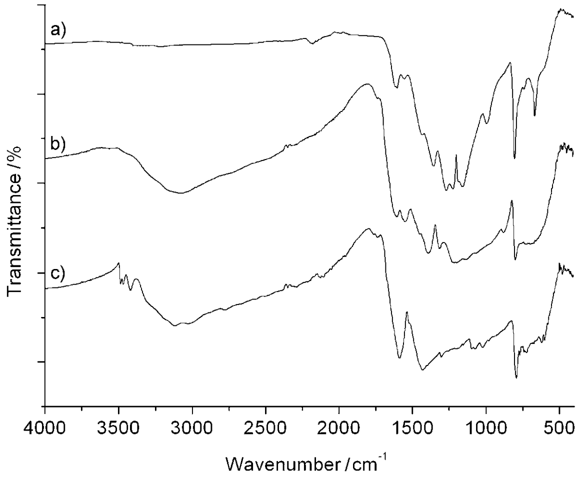

Figure 1. FTIR spectra of a) dicyandiamide prepared in molten salt, b) dicyandiamide prepared in the bulk and c) melem.

The progress of condensation via the bulk route compared with the salt-melt reaction are illustrated in Figure 2a and b, respectively. The products of both condensation routes show features at 1200 to 1600 cm^{-1} that are characteristic of aromatic CN heterocycles and also the breathing mode of the triazine units at 800 cm^{-1}. However, note that the stretching modes of secondary and primary amines and their intermolecular hydrogen-bonding interactions vanish almost completely for condensation products obtained from the salt melt at temperatures above 560 °C. This find supports the idea that the final condensation product obtained from the salt melt is devoid of terminal unreacted amino groups and is cohesive as an effect of covalent interactions rather than intermolecular hydrogen bonding.

The powder XRD pattern of graphitic carbon nitride obtained from thermal condensation of dicyandiamide in a

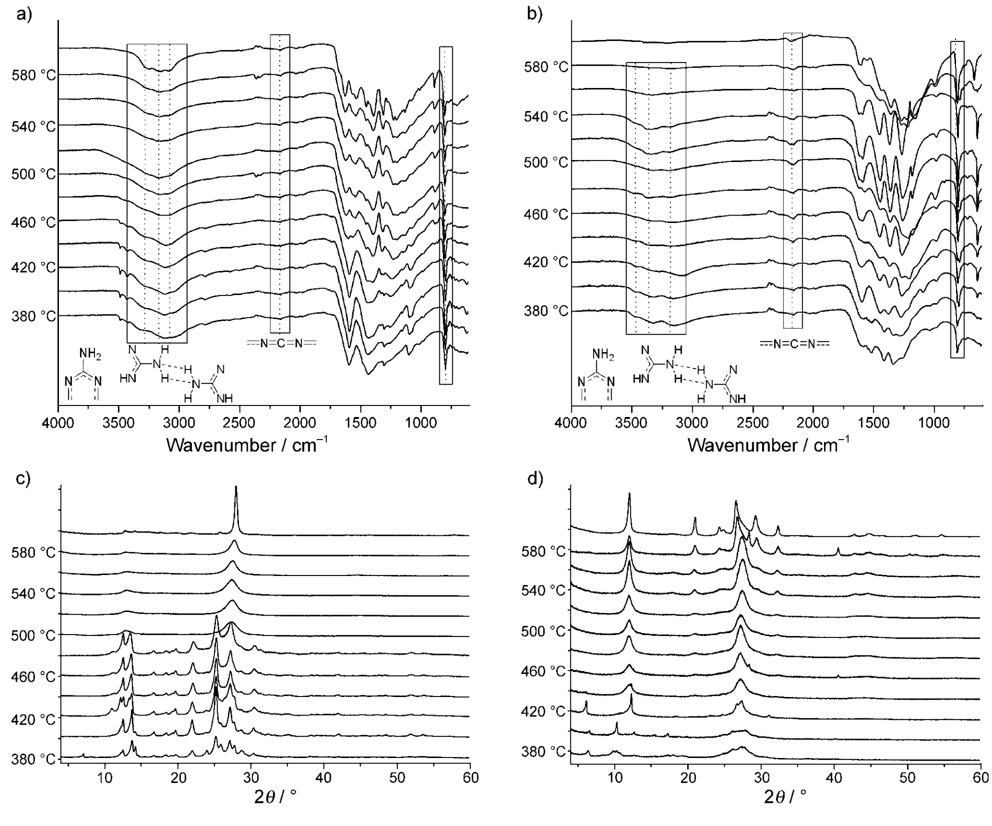

Figure 2. FTIR spectra of a) dicyandiamide prepared in the bulk and b) in molten salt and their respective powder XRD patterns (c,d).

molten salt was found to be well described by a hexagonal unit cell with the space group $P6_3cm$ (No. 185) with parameters $a=b=8.434$ Å and $c=6.722$ Å. The corresponding Bragg peak positions and systematic absences can be seen in Figure 3a and show an excellent correlation with the experimental powder XRD pattern. The difference plot (green) indicates an acceptable degree of fitting of the refined profile and of the previously calculated unit-cell parameters. The fit predicts average crystallite sizes of about 200 nm, which is corroborated by electron microscopy. Furthermore, a constrained LeBail refinement assuming homogenous crystallite sizes (i.e., the same full width at half maximum (FWHM) values) for peaks of the same phase confirmed that all indexed peaks are indeed part of one unique phase (Figure 3a).

The strongest peak at 26.5° is well known from discotic systems as the stacking peak of conjugated aromatic rings and was indexed as (002). This corresponds to an interplanar stacking distance of $d=3.36$ Å, a value which is comparable to the packing in crystalline graphite ($d=3.35$ Å).[32] Another pronounced peak is found at 12.1°, which corresponds to a distance $d=7.30$ Å and was indexed as (100). The structural motif giving rise to this reflection was confirmed by high-resolution transmission electron microscopy (TEM) as reported below, and it most likely corresponds to an in-plane arrangement of nitrogen-linked heptazine units, of which the ideal distance in a co-planar arrangement would be 7.3 Å with a layer-to-layer distance of 3.4 Å. (Figure 4a) The structure of the crystalline graphitic carbon nitride can be derived in analogy to graphite. The unit cell was populated with nitrogen-linked heptazine (C_6N_7) units that gave rise to graphitic C_3N_4 layers stacked in a staggered ABA fashion (Figure 4b). However, note that the chosen structural model is still simplistic because it assumes perfectly planar, fully aromatic C_3N_4 sheets and the absence of any stacking defects and neglects the admittedly small scattering contribution of lithium. In the light of the recent theoretical study by Senker et al. that suggested a corrugated conformation of individual graphitic carbon nitride sheets in g-C_3N_4,[33] it was not possible to investigate the nature of the dominant cohesive forces that seem to favour a perfectly planar arrangement of the graphitic sheets of the material reported herein. Taking into account the fact that residual amounts of Cl, K and Li were detectable by titration, even after extensive washing, it could not be unambiguously ruled out that intercalation of Cl, K and Li was not taking place and this could, in fact, be responsible for planarisation due to electronic ef-

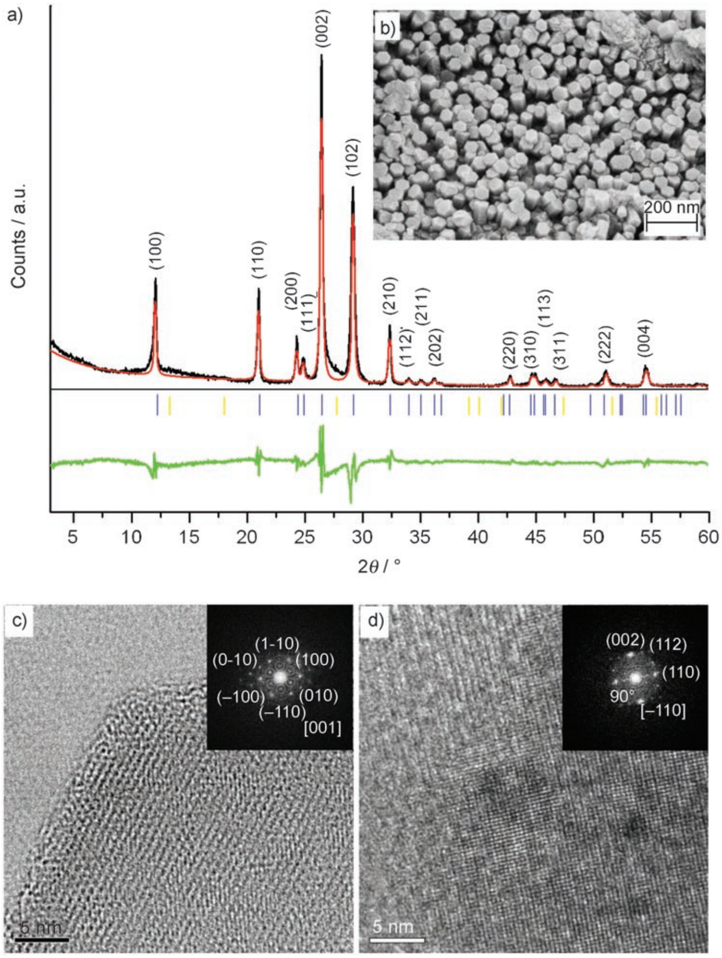

Figure 3. Physical characterisation of crystalline graphitic carbon nitride as obtained from the quartz glass ampoule (salt-melt reaction). a) LeBail decomposition and refinement performed on the XRD pattern of g-C_3N_4 with the observed pattern (——), the refined profile (——), the difference plot (——), Bragg peak positions (——) and reflections limited by the space-group symmetry (——). b) SEM image of g-C_3N_4. c),d) High-resolution TEM images showing a view in [001] direction and a view of the [−110] zone of g-C_3N_4, respectively.

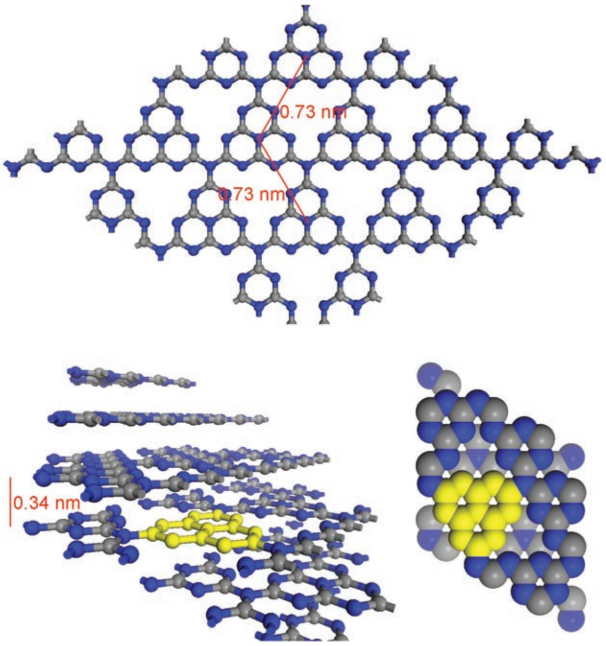

Figure 4. Proposed structure of crystalline graphitic carbon nitride as established by geometry optimisation using the Materials Studio Modelling software from Accelrys. Carbon and nitrogen atoms are represented as grey and blue spheres, respectively. A heptazine unit has been highlighted in yellow as a guide for the eye.

fects. The effects of Cl, K and Li and of a thermodynamically optimised C_3N_4 layer on the powder XRD pattern are still under investigation.

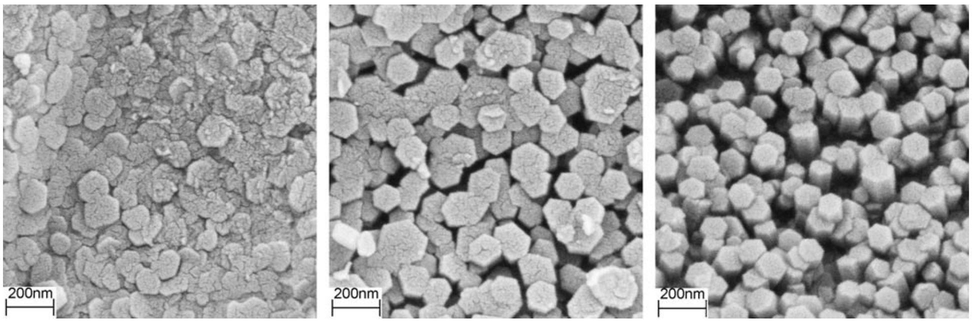

Figure 5. SEM images of crystalline graphitic carbon nitride prepared in molten salt, which show hexagonal prisms of increasing length, indicating that the z direction is the preferred direction of growth.

The progress of condensation via the bulk route was also monitored by using powder XRD and contrasted with the salt-melt reaction. The bulk route produces known condensation products of low molecular weight in the temperature region of 380 to 480 °C as described elsewhere,[7] and finally forms various oligomeric forms of Liebig's melon[34] from 500 °C onwards, as seen in Figure 2c. The terminal polymeric structure obtained by bulk condensation has two very distinct features, namely, peaks at 12.7° and 27.9°. Komatsu attributed the first peak to the (110) reflection of an orthorhombic melon with $a=7.396$ Å, $b=20.924$ Å and $c=12.954$ Å,[9] whereas Schnick et al. incorporated this peak as a (210) reflection of an orthorhombic melon with $a=16.7$ Å, $b=12.4$ Å and $c=3.2$ Å.[34] Nonetheless, both publications agree that the peak at 27.9° corresponds to a layered structural motif, namely, stacked chains of heptazine units linked by bridges of secondary amines.

The reaction in the salt melt progresses in a very different fashion (Figure 2d) The pronounced peak at 12.0°, which is thought to be a structural motif of a nascent sheet of planar carbon nitride, and the (001) reflection in a hexagonal unit cell that contains nitrogen-bridged heptazine units, are formed between 440 and 460 °C, that is, very early in the condensation process. Simultaneously, we observed the formation of a broad peak at around 27.1° that persists up to 580 °C. This peak can be attributed to a pseudo-(002) stacking motif of the nascent graphitic carbon nitride domains, similar to the turbostratic phase of graphite.[32] As the temperature increased (540–600 °C), peaks with a (**l) component became more pronounced and all visible peaks became sharper. At the same time, the FWHM value of the pseudo-(002) peak also decreased and moved to its final position at 26.5°. This can be rationalised by the increasing degree of condensation and thus an increase in crystallite size in all dimensions, especially through the stacking of extended graphitic carbon nitride sheets. Again, a study by scanning electron microscopy (SEM) confirms this find and shows hexagonal prisms of increasing length (Figure 5).

Samples of crystalline graphitic carbon nitride were sufficiently stable to allow high-resolution TEM and electron energy-loss spectroscopy (EELS) measurements. Figure 3c shows a view in the [001] direction on the edge of one of the hexagonal prisms visible in the SEM image. Measurements of the in-plane distance revealed a spacing of 7.25 Å at an angle of 60°, which corresponds to the spacing of coplanar, N-linked heptazine units and is in perfect agreement with the PXRD data. Figure 3d shows a view of the [−110] zone axis of g-C_3N_4. The two measured distances would, in this case, correspond to the (002) and (110) planes, which thus reveal the interlayer spacing of the heptazine units and the interplanar spacing already found with the corresponding XRD measurements. The EELS spectrum of the samples (Figure 6) shows that the system is composed of sp^2-hybridised carbon and nitrogen atoms, as indicated by the presence of a $1\,s\rightarrow\pi^*$ transition for both elements. The carbon-K-ionisation edge and nitrogen-K-ionisation edge show nearly identical near-edge structures, which indicates a similar threefold coordination electronic environment for both carbon and nitrogen in the synthesised material. Furthermore, the Cl-L-ionisation edge confirms the presence of residual chlorine, as established by elementary analysis. In addition, note that no energy loss due to oxygen could be detected, which corroborates the fact that the oxygen content established from elemental microanalysis cannot be attributed to an intrinsic structural component of the product.

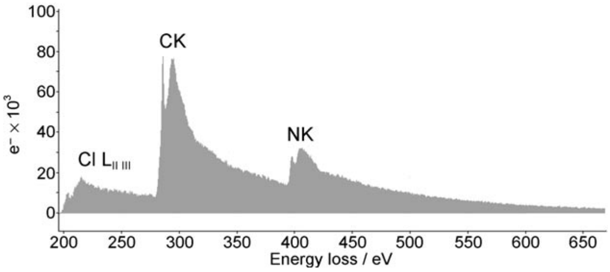

Figure 6. EELS spectrum of carbon and nitrogen K edges, recorded for g-C_3N_4.

Conclusion

The formation of highly crystalline graphitic carbon nitride by a simple self-condensation of dicyandiamide in a salt melt of lithium chloride and potassium chloride has been demonstrated and the resulting g-C_3N_4 was compared with Liebig's melon as formed by the traditional bulk condensation route. FTIR and elemental analysis of the product hint at a structure with few defects and few unreacted end groups and, therefore, an extensively condensed framework. Powder XRD analysis and high-resolution TEM show the presence of pronounced in-plane ordering with a repeat distance of $d = 7.30$ Å, which corresponds to the separation of co-planar, covalently linked heptazine units, and a planar graphitic interlayer distance of $d = 3.36$ Å. On this basis, we propose that the structural model for the material obtained is based on extended sheets of covalently linked *s*-heptazine (C_6N_7) units that stack in a graphitic fashion, which supports the predictions of Kroke et al.[22]

Regarding the potential of this material, it should be noted that a better understanding and control of the condensation and crystallisation process of g-C_3N_4 holds the key to manufacturing semiconducting materials of the carbon nitride type with band gaps of tuneable size. Such a material could find applications in the fields of lasers and photocatalysts, to name just two. Other work focuses on the actual application of the very unusual catalytic behaviour of graphitic carbon nitride[18–20] and the possibility of creating intercalation compounds of g-C_3N_4 that are analogous to graphite.

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