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Attempted chemical synthesis of graphite-like carbon nitride

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Melamine-based quasi carbon nitride with an orthorhombic layer structure and a molecular weight of more than *m*/*z* 5000 was prepared with a system of melamine–Lewis acid at 600–700 °C in an autoclave avoiding catalytic carbonation action by ferrous substances.

Graphite-like C_3N_4 materials (g-C_3N_4) have recently attracted much attention for their potential for organic semiconductors and the precursors of hypothetical superhard β-C_3N_4. Four types of g-C_3N_4 have been presented: the final de-ammonation product of melon which Franklin predicted and attempted to synthesize;[1,2] the fused heterocyclic material by Redemann and Lucas in which the vacancy of melon is filled by three carbons and one nitrogen atom;[2] the melamine-based carbon nitride introduced by Teter and Hemley which is formally depicted as a perfect de-ammonation polycondensate of melamine;[3] and the triazine-based carbon nitride prepared by polycondensation of melamine in a hydrazine solvent under supercritical conditions by Alves *et al.*[4] The structure models of the carbon nitrides are depicted in Fig. 1. Most of them are still not completely confirmed because of difficult problems in the synthesis. Recently, examples of a new type of high-heat-resistance carbon nitride were prepared from several tri-functional tris-*s*-triazine derivatives; however, the stoichiometric N : C ratios were much smaller than 1.33 for C_3N_4.[5] Different from these carbon nitrides, melamine gave related compounds such as melon,[6] poly(aminomethineimine),[7] melamine–cyanuric chloride copolymers and nitrogen-containing disordered carbon. However, these derivatives could not be chemically changed into carbon nitride after all. Melamine would be most suitable for manufacturing g-C_3N_4 if one could achieve complete de-ammonation/polycondensation, which is very difficult because of the weak basicity of melamine. This work reports an attempt at the chemical synthesis of melamine-based carbon nitride by polycondensation of melamine using a Lewis acid such as $ZnCl_2$.

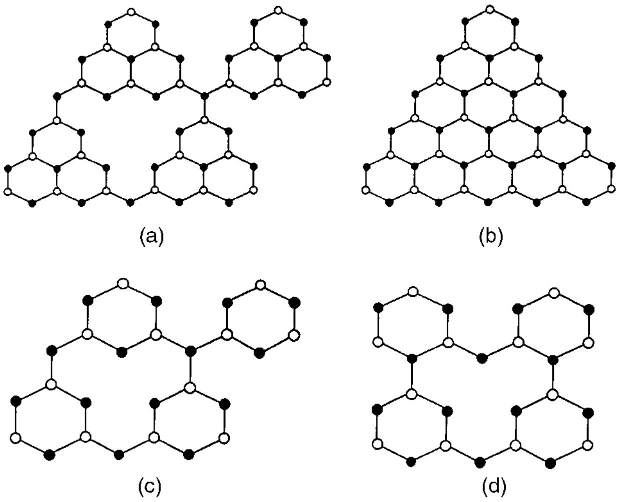

Fig. 1 The structure models of the graphite-like carbon nitrides: ○, C atom; ●, N atom; (a), Franklin's model; (b), Redemann's model; (c), Teter's model; (d), Alves's model.

Experimental

A mixture of melamine (8.0 g) and $ZnCl_2$ (8.0 g) was placed into an alumina tube, sealed with $CaCl_2$ powder on top, inserted into an autoclave and heated to 650 °C for 1 h. The residue was washed with boiling water, boiled in 35% HCl to remove unchanged starting material and zinc compounds, purified by boiling in 3 M KOH and successively with 35% HCl, washed with boiling water and vacuum-dried at 200 °C. A pale ocher powder was obtained, yield 5.6 g. Anal. Found: C, 37.11; H, 1.84; N, 61.05%. $\rho = 1.907$ g cm^{-3}.

X-Ray powder diffraction was conducted with Cu-Kα radiation generated at 40 kV–200 mA in the 2θ range 4–100° and at a scanning speed of 0.1 ° min^{-1}. Density was measured by the sink–float method in a dibromomethane–ethanol solution whose density was determined pyknometrically. Mass spectra were run on a matrix-assisted laser-desorption-mass-spectrometer. Ionization was performed with a Nd–YAG laser (355 nm) without matrix.

Results and discussion

Prior to this work, de-ammonation reagents of melamine were searched for. Anhydrous $CaCl_2$ and several Lewis acids such as $ZnCl_2$, $SnCl_2$ and $AlCl_3$ were effective. These reagents coordinate to melamine upon dissolution or melting and eliminate ammonia from the complexes at elevated temperatures. It has been reported that a system of melamine–Lewis acid at 350–500 °C in an autoclave undergoes ring-opening polymerization of melamine to produce brownish black powders of linearly conjugated poly(aminomethineimine).[7] However, re-examination showed that the system produces a considerable amount of carbonaceous byproducts at temperatures above 450 °C because of the catalytic carbonization action by metallic iron and ferrous substances contained within a stainless steel autoclave. Surprisingly, the present reaction system avoiding contact with ferrous substances gave quasi carbon nitride composed of triazine rings but not poly(aminomethineimine), as elucidated in the following.

Chemical analysis and IR spectra

Alkaline hydrolysis of the material by boiling in 6 M KOH gave only 6-amino-2,4-dihydroxy-1,3,5-triazine in addition to

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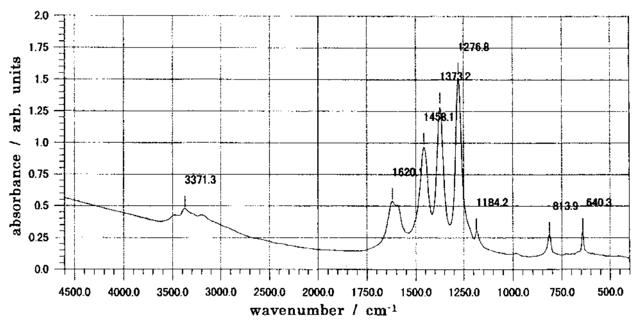

Fig. 2 IR spectrum of the material obtained. Several very weak peaks around 3371 cm^{-1} are due to $\nu(NH_2)$ and ν(NH). A very weak peak at 1184 cm^{-1} is unassigned. A weak peak at 640 cm^{-1} is a new peak that is unobserved for melamine and its linear polymers.

gaseous ammonia. Acid hydrolysis by boiling in 6 M HNO_3 followed by treatment with an alkaline cupric ammonium sulfate solution resulted in precipitation of an amethyst-red cyanuric acid–copper complex.[8] The results show the materials to consist of triazine rings. Also from a N : C atomic ratio of 1.41, structures consisting of $C_3N_3(NH)_{1.5}$ and $C_3N_3(N)$ units are suggested. The NH and and $\rangle$N– groups are clearly observed with strong IR peaks at 1277 and 1373 cm^{-1} which are generally assigned to ν(C–N) of aromatic secondary and tertiary amines, respectively (Fig. 2). An extraordinarily high absorbance of ν(C–N) compared to ν(ring) at 1458 cm^{-1} indicates a network structure of triazine rings cross-linked with NH and $\rangle$N– groups.

Mass analysis

The mass spectrum of the material showed fragments over *m*/*z* 5000 (Fig. 3). The spectrum is formally divided into four blocks: *m*/*z* 112–161, 246–888, 1056–1344 and 1344–5028. The first block contains fragments of diaminotriazine (*m*/*z* 112) and melamine (*m*/*z* 128) but no fragments of *m*/*z* 186 and 202, which are expected for melon. The second contains a repeating unit of *m*/*z* 109 such as *m*/*z* 246–355, 355–464, 293–402, 402–511 and 536–645. This unit is assigned to the fragment $C_3N_3(NH_2)(NH)$. The third block consists of fragments having intervals of *m*/*z* 24–288, equal to an integral multiple of *m*/*z* 24. One of the intervals, *m*/*z* 120, attributable to a fragment of $C_3N_3(N)_3$ (appearing with *m*/*z* 121 in the first block), is noted, since this fragment originated from the large mass block in contrast to *m*/*z* 109 from the small one. That is, the network is terminated with $C_3N_3(NH_2)(NH)$ bonds at the fringes and consists of $C_3N_3(N)$ bonds in the inside. Different from this, a network of the $C_3N_3(NH)_{1.5}$ unit (a theoretical N : C = 1.5 : 1) may be supposed. However, this structure is very improbable because there are no fragments repeating with an interval of *m*/*z* 309 or 294.

X-Ray powder diffraction

A structure unit of the network was further clarified by X-ray powder diffraction since the material gave a polycrystalline pattern (Fig. 4). As a result of indexing, the pattern was assigned to an orthorhombic system having a lattice constant of $a = 0.7300$, $b = 0.8467$ and $c = 0.6492$ nm and a unit cell volume of 0.4012 nm^3 (Table 1). Many of the diffraction lines in Fig. 3 show tailing towards larger 2θ values. This is typical for turbostratic disorder in layered materials. From the unit cell volume and a density of 1.907 g cm^{-3}, a total atomic mass of 460 is estimated. This mass is equal to five times the mass of C_3N_4 ($M_w = 92$). The number of atoms in the unit cell is smaller than that estimated from Teter's structure model[4] of g-C_3N_4 by six, and the observed density is 87% of the theoretical density.[4] The large deviations from the perfect g-C_3N_4 are well explained by a structure model which has another large vacancy capable of containing one triazine ring in addition to the usual carbon-vacancy, as shown in Fig. 5. Again back to the mass spectrum, the fragments of *m*/*z* 1855, 2350, 2766 and 3311 may be corresponding to four, five, six and seven pieces of the unit cell.

Reaction mechanism

An alternative method, heating the starting mixture to 600–700 °C in an oven, produces the same material at a yield of 30–40% and a considerable amount of the byproduct melamine–hydrochloride salt which volatilizes in this temperature range. The material production at high yields (60–70%) in an autoclave may be due to highly concentrated chlorine

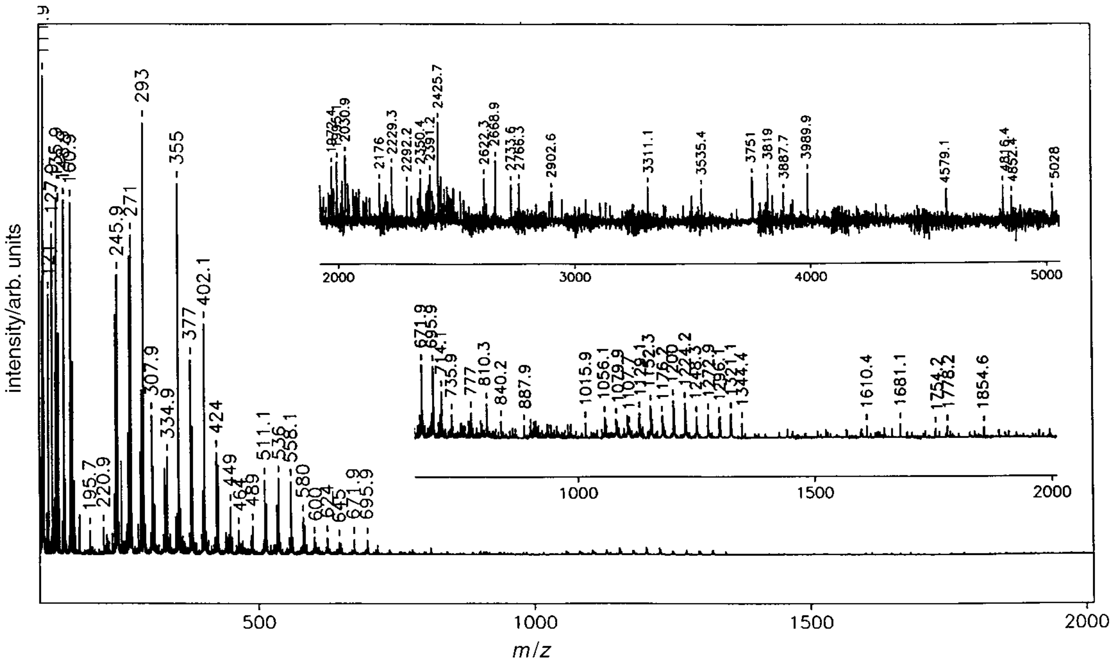

Fig. 3 Mass spectrum of the material. The repeating unit *m*/*z* 109 contained in the range *m*/*z* 246–888 corresponds to $C_3N_3(NH_2)NH$ and the interval *m*/*z* 120 between fragments in the range *m*/*z* 1056–1344 corresponds to $C_3N_3(N)_3$.

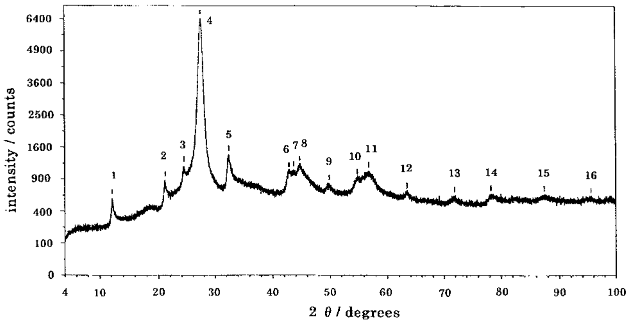

Fig. 4 X-Ray powder diffraction pattern of the material.

originating from zinc chloride. A conceivable reaction mechanism in the closed system is:

$$n\,C_3N_3(NH_2)_3 \xrightarrow[600-700\,^{\circ}C]{ZnCl_2} n\,C_3N_4\ \text{(zinc complex)} + 2n\,NH_3\ \text{(possibly chloride)}$$

where the product, as received and washed only with boiling water, was confirmed to be a chlorine-free C_3N_4–zinc complex by IR, elemental analysis and X-ray photoelectron spectroscopy. The complex was treated with HCl to remove the coordinate zinc and then successively with a KOH solution. The material obtained is insoluble, infusible and thermally stable to 600 °C; however, it reacts with alkaline cupric ammonium sulfate solution producing a dark green copper complex. Since a sample weight measured after the reaction had increased by more than 50% of the initial weight, the copper ions must be caught in the large vacancy. The method developed in this work is a simple and easy one-pot reaction and gives quasi graphite-like carbon nitride with a molecular mass of more than *m*/*z* 5000. Although the material is not perfect C_3N_4, it may be used for a model compound of g-C_3N_4.

Table 1 Interplanar spacings for sample A

Peak number	2θ/ degrees	Ortho- rhombic *hkl*	Observed *d* values/ nm	Calculated[a] *d* values/ nm	Difference
1	12.121	100	0.7296	0.7300	+0.0004
2	21.093	111	0.4208	0.4208	±0.0000
3	24.389	200	0.3646	0.3650	+0.0004
4	27.456	002	0.3246	0.3246	±0.0000
5	32.404	220	0.2761	0.2763	+0.0002
6	42.682	040	0.2117	0.2114	−0.0003
7	43.667	103	0.2071	0.2075	+0.0004
8	44.641	140	0.2028	0.2031	+0.0003
9	49.767	240	0.1831	0.1830	−0.0001
10	56.794	004	0.1620	0.1623	+0.0003
11	63.346	152	0.1467	0.1469	+0.0002
12	71.752	512	0.1314	0.1315	+0.0001
13	78.156	360	0.1222	0.1223	+0.0001
14	82.132	171	0.1173	0.1172	−0.0001
15	87.347	460	0.1115	0.1115	±0.0000
16	95.230	700	0.1043	0.1043	±0.0000

[a] Calculation is based on the orthorhombic parameters $a = 0.7300$, $b = 0.8467$ and $c = 0.6492$ nm.

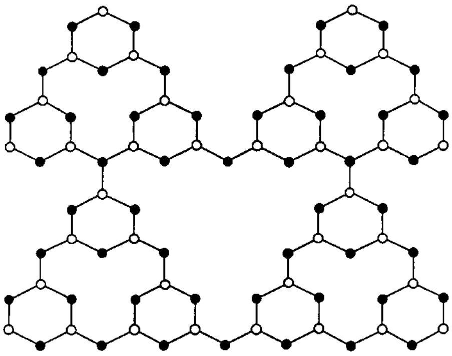

Fig. 5 Structure unit of the material: ○, C atom; ●, N atom. The structure is analogous to Teter's model of g-C_3N_4 except for a large vacancy surrounded by six C_3N_4 units.

Conclusions

A reaction system of melamine–Lewis acid was examined for the preparation of graphite-like carbon nitride. It was found that heating a mixture of melamine and $ZnCl_2$ to 600–700 °C in an autoclave produced a high yield of de-ammonation/polycondensation materials of melamine, upon avoiding catalytic carbonization action by ferrous substances. The results of IR spectroscopy, chemical analysis, mass analysis and X-ray powder diffraction elucidated that the material is a polycrystalline quasi carbon nitride having a unique vacancy-network structure consisting of triazine nuclei, a molecular mass of more than *m*/*z* 5000 and terminal NH_2 and NH groups.

Acknowledgements

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References

1 E. C. Franklin, *J. Am. Chem. Soc.*, 1922, **44**, 486. Melon is known as an ill-defined polymer (first observed by Berzelius and named by Liebig) that is left after the ignition of mercuric thiocyanate. Franklin carried out extremely cautious heating of mercuric thiocyanate to obtain impure specimens of carbon nitride..

2 C. E. Redemann and H. J. Lucas, *J. Am. Chem. Soc.*, 1940, **62**, 842. Two structures are assigned to melon: a linear form from de-ammonation/polycondensation of 2,5,8-triamino-tris-*s*-triazine and a symmetric triangular form from de-ammonation ring-closure of three molecules of 2,5,8-triamino-tris-*s*-triazine. Redemann and Lucas assigned Franklin's carbon nitride specimens to the latter form of melon..

3 D. M. Teter and R. J. Hemley, *Science*, 1996, **271**, 53.

4 I. Alves, G. Demazeau, B. Tanguy and F. Weill, *Solid State Commun.*, 1999, **109**, 697.

5 T. Komatsu and T. Nakamura, *J. Mater. Chem.*, 2001, **11**, 474.

6 V. V. Khorosheva and A. I. Finkel'shtein, *Zh. Fiz. Khim.*, 1962, **36**, 1055.

7 V. R. Mkrtychan, A. F. Lunin and Ya. M. Pauskin, *Vyskomol. Soedin., Ser. A*, 1969, **11**, 866.

8 C. E. Redemann and H. J. Lucas, *J. Am. Chem. Soc.*, 1939, **61**, 3423.