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Template assisted formation of micro- and nanotubular carbon nitride materials

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Abstract

Micro- and nanotubes of an amorphous carbon nitride material were synthesized by metathesis reactions between cyanuric chloride $(C_3N_3Cl_3)$ and different nitrogen sources, such as Li₂(CN₂) or Li₃(BN₂). The intermediate formation of needle-shaped crystals of N(C₃N₃Cl₂)₃ was always observed in our reactions, and investigated with respect to their role as a template in the formation of tubes. Chemical analyses of the micro- and nanotubes reveal carbon to nitrogen ratios near 3:4, consistent with the suspected material C₃N₄. Synthesized carbon nitride materials were thermally stable up to 600 °C in inert atmosphere. They were inspected by a number of physical measurements, mainly using TEM, EDX and IR investigations.

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1. Introduction

The search for C_3N_4 , the third binary compound of the B–C–N system besides the well-known compounds BN and B₄C, has become a great challenge among scientists worldwide. Theoretical studies predict over 20 C_3N_4 -phases to be metastable at ambient conditions. Numerous research efforts, recently reviewed by Kroke and Schwarz [1] and Malkow [2], have been made in this field, often motivated by the prediction of very high bulk and shear moduli for some saturated C_3N_4 phases, and their potential applications as hard materials but also by other possible applications, e.g. as hydrogen storage [3] or flame-retardant materials [1,4].

Besides 3-dimensional C_3N_4 -structures with sp³-hybridized carbon, graphite-like structure models are also proposed. These structures usually are considered to contain planar networks of nitrogen-connected s-triazine [5–9], or tri-s-triazine (heptazine)

moieties [10–13]. The two most frequently discussed structure proposals for g-C₃N₄ are displayed in Fig. 1. The arrangement of [N(C₃N₃)] and [N(C₆N₇)] building blocks in a layer-type network structure should be detectable by the appearance of 00l reflections, representing the average layer-to-layer distance. Non-planar networks based on triazine moieties have also been considered, for example by Yaghi et al. who derived from their calculations that these 3-dimensional networks should be more stable than their planar analogues [14].

The synthesis of these interesting materials with the target composition C_3N_4 has been approached by a great number of different methods. But the characterization remains difficult due to the low crystallinity or inhomogeneity of the resulting materials, so that the existence of the predicted C_3N_4 -phases cannot be unambiguously evidenced. However, the increasing number of reports on carbon nitrides accounts for the existence of new materials in this field of research [5–8,15–18]. Yet more work is necessary to establish this material and to investigate its potential. Besides a high-yield, high-purity synthesis, a better understanding of formation mechanisms is desirable.

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Fig. 1. Nitrogen-bridged s-triazine $[N(C_3N_3)]$ (top) and tri-s-triazine $[N(C_6N_7)]$ (bottom) units as possible building blocks of $g-C_3N_4$ structures.

Our research on C_3N_4 started with reactivity studies of lithium dinitridoborate $Li_3(BN_2)$ or lithium carbodiimide $Li_2(CN_2)$ with transition metal chlorides. Reactions with TiCl₃, NbCl₅ and NiCl₂ caused partial decompositions of the ions $(BN_2)^{3-}$ and $(CN_2)^{2-}$ and yielded transition metal nitrides, LiCl and BN or in case of $(CN_2)^{2-}$, an amorphous brownish phase addressed as a carbon nitride [19].

In this work we report studies of metathesis reactions of cyanuric chloride $C_3N_3Cl_3$ with various solid nitrogen sources, using alkali carbodiimides ($Li_2(CN_2)$, $Na_2(CN_2)$), sodium di-cyanamide ($Na[N(CN)_2]$), lithium di-nitridoborate ($Li_3(BN_2)$), lithium nitride (Li_3N), or cyanamide, (H_2NCN). In early stages of all of these reactions, the formation of the intermediate $N(C_3N_3Cl_2)_3$, featuring three triazine rings linked by a nitrogen atom, can be evidenced. Later on, the reactions yield micro- and nanotubes of brown, amorphous materials with compositions close to C_3N_4 . Our experimental findings indicate that crystals of $N(C_3N_3Cl_2)_3$ serve as a template for the formation of the carbon nitride tubes.

2. Experimental section

2.1. Synthesis

Metathesis reactions were performed between cyanuric chloride and several solid nitrogen sources, such as $Li_2(CN_2)$, $Na_2(CN_2)$, $Na[N(CN)_2]$, $Li_3(BN_2)$, Li_3N , and H_2NCN . The reactions were carried out as salt balanced metathesis reactions, following the principal reaction strategy:

$$C_3N_3Cl_3 + A_3N \rightarrow C_3N_4 + 3ACl.$$

All reactants were handled inside a glove box under dry argon. The reactions were performed in silica ampoules which were filled under argon and then sealed under vacuum. Lengths and inner diameters of normally used silica ampoules were 6–7 cm and 0.7 cm, respectively.

Cyanuric chloride (Aldrich, 99%) was sublimed under vacuum at 90 °C for purification. Li₂(CN₂) was prepared from Li₂CO₃ and ammonia according to the method of Perret [20]. For the synthesis of Li₃(BN₂), Li₃N and α -BN were reacted at 800 °C in sealed copper ampoules [21]. Na₂(CN₂) was made from NaHCN₂ and NaNH₂ [22]. Commercially available Na[N(CN)₂] (ABCR, 96%), Li₃N (Alfa Aesar, 99.5%), and H₂NCN (Fluka, 98%) were used without further purification. The typical amount of reactant mixture was around 200–300 mg per ampoule.

The ampoules were slowly heated and kept at temperatures between 250 °C and 350 °C for 10–24 h. Afterwards the temperature was further raised to about 500 °C, and the samples remained at this temperature for 1–3 weeks, before the ampoules were cooled to room temperature within 2–3 days.

During the heating process, a colorless melt of cyanuric chloride was always formed near 150 °C. On further heating the melt became more viscous and turned yellow in color. Above 200 °C alkali metal chloride and N(C₃N₃Cl₂)₃ [14,23] were identified as crystalline products, according to powder and single crystal XRD measurements, respectively. Crystals of $N(C_3N_3Cl_2)_3$ were growing as bunches of long, thin needles from the wall of the silica ampoule. Later on, during the final stage of the reaction, brownish micro- or nanotubes of a carbon and nitrogen containing material were obtained. A similar material also deposited on the wall of silica ampoules as a thin layer, ranging from red to brown in color. In addition, a dark pellet of solidified melt was found in the lower part of the ampoule when cyanuric chloride was reacted with lithium salts. The pellet was composed of LiCl along with some amorphous material, according to powder XRD measurements. The diameter of the tubes depended on several factors, such as the reaction counterparts and heating and cooling rates. In our reactions we found diameters ranging between 100 nm and 7 µm and lengths of tubes up to 1 mm.

The products from the as-described reactions occur as brittle materials with colors ranging from red to brown. When Li_3N was employed as nitrogen source, the products were slightly darker in color than those from reactions of $Li_2(CN_2)$ or $Li_3(BN_2)$ with $C_3N_3Cl_3$. Mixtures of Li_3N and cyanuric chloride turned out to be explosive if the reactants were heated up too fast. Reactions with $Na_2(CN_2)$ or $Na[N(CN_2)]$ yielded NaCl and yellowish brown amorphous materials. The tubes obtained from reactions with sodium salts were generally smaller in diameter than those obtained from lithium salts. Reactions of H_2NCN and $C_3N_3Cl_3$ gave HCl and brown tubes of carbon nitride material along with layer-like material and a brown, porous pellet in the lower part of the ampoules.

The tubes were separated mechanically and usually washed with water and acetone. The material was then dried in air and used for different studies and measurements.

 $N(C_3N_3Cl_2)_3$ was synthesized by reacting $C_3N_3Cl_3$ and 2amino-4,6-dichloro-1,3,5-triazine (molar ratio 1:2) in closed silica tubes at 200 °C. The raw product was heated under vacuum at 100 °C for several hours in a sublimation apparatus to remove unreacted starting materials. For further purification, $N(C_3N_3Cl_2)_3$ was sublimed in a silica ampoule.



Fig. 2. Carbon nitride tubes synthesized from C₃N₃Cl₃ and Li₃(BN₂).



Fig. 3. $N(C_3N_3Cl_2)_3$ crystal together with a drawing of the molecular structure (left), and scanning electron micrograph of a single carbon nitride tube made from Li₃(BN₂) and C₃N₃Cl₃ (right).

2.2. Characterization

Scanning electron microscope (SEM) images were recorded using a Philips XL 30 and a Jeol JSM-6500F, respectively. Transmission electron microscope (TEM) and EDX measurements were carried out on a Philips CM 30 ST electron microscope (300 kV, LaB₆ cathode, Gatan multiscan CCD camera) equipped with a Noran Si-Li detector for EDX analyses. Chemical combustion analyses for the quantitative determination of hydrogen, carbon and nitrogen were performed using an Elementar vario EL II elemental analyzer. Chlorine contents were determined by pulping the materials following the method of Schöninger, followed by titration with Hg(ClO₄)₂ using diphenyl carbazon as an indicator. Vibrational spectra were recorded on a Perkin Elmer FTIR-spectrometer (Spectrum 1000) in a range from 4000 to 200 cm^{-1} using KBrpellets. The thermal behavior was studied by DTA/TG measurements (Netzsch, simultaneous thermal analyser, 409C), carried out in sealed silica ampoules or in Al₂O₃ crucibles usually in the temperature interval between 20 and 600 °C. For combined TG/MS examinations a Netzsch STA 409 thermal analyser and a quadrupole mass spectrometer (Balzers QMG 421) were used. For X-ray analyses, a Stoe Stadi-P powder diffractometer and a Stoe IPDS single crystal diffractometer were used.

3. Results and discussion

3.1. Microscopic examinations

3.1.1. Light-optical microscope and SEM

The products of the as-described reactions of $C_3N_3Cl_3$ and nitrogen-sources were examined by light-optical (Fig. 2) and scanning electron microscopes, revealing that some of the tubes possess a hexagonal inner profile. Single crystals of $N(C_3N_3Cl_2)_3$ (space group $R\bar{3}$) were found to have the shape of



Fig. 4. Scanning electron micrographs of a filled microtube.



Fig. 5. Transmission electron micrograph of a tube synthesized from $C_3N_3Cl_3$ and $Li_3(BN_2)$, used for EDX measurements to compare filled and empty regions.

long, thin, hexagonal prisms and are therefore assumed to be the framework for the tubes in early stages of the reactions. Fig. 3 shows one of these single crystals and a microtube synthesized from $Li_3(BN_2)$ and $C_3N_3Cl_3$. In some SEM images filled microtubes can be seen which possibly still contain residues of $N(C_3N_3Cl_2)_3$ or a decomposition product of the template material (Fig. 4).

3.1.2. TEM

Transmission electron microscope examinations of the tubes also revealed that some of them are partially filled with another material (Fig. 5). EDX spectra taken from different spots in the central area of a tube, displayed in Fig. 5, show significantly varying chlorine contents. When filled regions were compared with empty regions, a significant Cl-content was obtained in the filled areas, suggesting a Cl-rich filament to be present.

In addition, the distributions of the elements C, N and Cl were determined by element-mapping experiments on a microtube. In contrast to a homogeneous distribution of carbon and nitrogen in the periphery, the chlorine is located in the core of the tube, indicating Cl-containing compounds such as $N(C_3N_3Cl_2)_3$ or its decomposition products being present in the core of a carbon nitride tube (Fig. 6). Electron diffraction experiments gave no indication of crystalline residues and therefore confirmed the amorphous character of the tubes.



Fig. 6. Distribution of carbon (bottom left), nitrogen (bottom right) and chlorine (top right) in a carbon nitride tube synthesized from H_2CN_2 and $C_3N_3Cl_3$, and a SEM image of the analyzed carbon nitride tube (top left).

3.2. Chemical analysis

Chemical combustion analyses were performed for three samples (A-C), which were synthesized from cyanuric chloride with different reactants yielding C/N weight ratios between 0.605 and 0.698 (0.643 calc. for C_3N_4). Sample A was prepared from Na₂(CN₂) and C₃N₃Cl₃ at 480 °C and subsequently washed with water and acetone to remove NaCl and possible residues of unreacted starting materials. For the preparation of sample **B** lithium cyanamide and C₃N₃Cl₃ were reacted at 550 °C. The obtained material was likewise washed with water and acetone. Sample C was synthesized from H₂NCN and C₃N₃Cl₃ at 500 °C. Unreacted cyanamide and cyanuric chloride were removed by sublimation at 100 °C under vacuum, and the chemical composition was determined immediately, without further washing of the sample to avoid oxygen contamination. Table 1 summarizes the results of the chemical analyses for the samples A-C.

The analyzed C/N weight ratios of the samples were all close to the theoretical value for C_3N_4 ; however, the sum of the C and N contents of samples **A** and **B** were significantly below 100%. In contrast, sample **C**, made from H₂CN₂ and C₃N₃Cl₃, still contained a large amount of Cl. The low totals for the samples **A** and **B** may result from adsorbed residues of water inside or on the surface of the tubes.

3.3. Infrared measurements

Infrared spectra of carbon nitride materials resulting from reactions of cyanuric chloride with cyanamide (H₂NCN), lithium cyanamide (Li₂(CN₂)), and lithium nitridoborate (Li₃(BN₂)), respectively, were measured. To remove possible residues of unreacted reagents, all samples were heated to 100 °C under dynamic vacuum for several hours. The spectra

Table 1 Results of the chemical analyses in wt%

	Sample A	Sample B	Sample C
C	29.5	30.0	30.9
N	48.8	43.0	44.2
Н	2.6	2.8	0.5
Σ	80.9	79.9	99.4
C/N ratio	0.605	0.698	0.698



Fig. 7. Infrared spectra of carbon nitride materials synthesized from reactions of $C_3N_3Cl_3$ with $H_2(CN_2)$ (a), $Li_2(CN_2)$ (b), and $Li_3(BN_2)$ (c), respectively.



Fig. 8. Comparison of the infrared spectra of a carbon nitride material obtained from a reaction of $C_3N_3Cl_3$ and $Li_3(BN_2)$ (bottom), and of $N(C_3N_3Cl_2)_3$ (top).

reveal multiple, almost identical absorption bands in the region between 1600 and 800 cm⁻¹. Strong, broad absorptions are detected at 1615 and 1330 cm⁻¹; medium to weak, sharp absorptions appear at 1550, 1515, 1213, 1180, 1094, 946, and 824 cm⁻¹ (Fig. 7). Fig. 8 shows a comparison of the IR spectra of the material obtained from the reaction of C₃N₃Cl₃ and Li₃(BN₂) with the intermediate product N(C₃N₃Cl₂)₃. Several absorption bands observed for N(C₃N₃Cl₂)₃ do not occur in the spectrum of the final carbon nitride material. Therefore, it is unlikely that the carbon nitride material still contains significant amounts of N(C₃N₃Cl₂)₃. However, absorptions at 1550, 1515 and 1094 cm⁻¹ are found in both spectra at almost the same position and might be assigned to stretching modes of the triazine ring (1550 and 1515 cm⁻¹) [24] and to a NC₃ stretching mode of tertiary amines (1094 cm⁻¹) [25]. The two strong, broad absorptions at 1615 and 1330 cm⁻¹ are remarkably similar to absorptions in vibrational spectra published for the heptazine compounds $C_6N_7Cl_3$ and $C_6N_7(N_3)_3$ [26]. Absorptions in these regions (at 1606 and 1304 cm⁻¹) are also reported for tri-aminoheptazine or melem $C_6N_7(N_2)_3$ [10,27]. Therefore, these absorption bands could be due to vibrations of a heptazine framework.

Numerous publications concerning triazine compounds describe a sharp, medium strength vibration near 816 cm⁻¹ as being characteristic for the triazine nucleus [28–33]. Thus, the absorption at 824 cm⁻¹ observed in our spectra of tubular CN compounds can be interpreted as an out-of-plane deformation mode of the C_3N_3 ring. On the other hand, infrared spectra of compounds containing heptazine nuclei also exhibit an absorption signal in this region [10,26,27].

The IR spectra of our tubular carbon nitride materials obviously show vibrational signals typical for the triazine as well as for the heptazine framework. However, experimental data for triazine and heptazine compounds reveal absorption bands in similar or overlapping regions of the spectra, making a clear differentiation between both heterocyclic frameworks quite difficult. The formation of heptazine nuclei from cyanuric chloride as a starting material and therewith their existence in the obtained tubular materials seems unlikely at first glance, however, it can be deduced from the decomposition behavior of N(C₃N₃Cl₂)₃, as we shall describe later.

3.4. Thermal analysis and TG/MS

When carbon nitride tubes synthesized from cyanuric chloride and lithium cyanamide were investigated via DTA/TG with a heating rate of 5 °C/min, weight losses were monitored at 600 °C in air or at 650 °C under argon. A combined TG/MS examination was carried out between RT and 800 °C under Ar applying a heating rate of 10 °C/min. Above 500 °C decomposition products such as (CN)₂, CN and C were detected. Additionally, the release of fragments with m/z ratios corresponding to C₂N and N₂ were detected at temperatures above 630–650 °C. After the TG/MS experiment, a light grey, hygroscopic residue (approx. 30 wt% of the starting material) was obtained.

3.5. Formation and thermal stability of $N(C_3N_3Cl_2)_3$

 $N(C_3N_3Cl_2)_3$ was first described in 2003 by Yaghi et al. who obtained crystals of this compound from cyanuric chloride and lithium nitride at 250 °C [14].

The formation of colorless needle-shaped crystals of $N(C_3N_3Cl_2)_3$ is observed in all of the performed reactions at temperatures between 200 and 250 °C, clearly indicating that it is a vital intermediate of reactions between cyanuric chloride and nitrogen sources. For a better understanding of its thermal behavior, investigations of X-ray pure $N(C_3N_3Cl_2)_3$ were carried out in sealed silica ampoules.

Sublimation of $N(C_3N_3Cl_2)_3$ occurs near 320 °C, evidenced by an endothermic DTA signal of a sample in a sealed sample holder, as well as by the visible growth of needleshaped crystals in the colder section of a reaction ampoule. On heating $N(C_3N_3Cl_2)_3$ above 400 °C, a light brown amorphous material starts to deposit at the inner wall of the silica ampoule. In addition, yellow plate-like crystals were obtained and characterized afterwards by single crystal X-ray diffraction as the condensed heterocyclic compound heptazine chloride $C_6N_7Cl_3$ [34].

3.6. Discussion

Except for the reactions including $Li_3(BN_2)$, all reaction equations can be formulated yielding C_3N_4 and alkali metal chlorides or HCl, as illustrated for $Li_2(CN_2)$ and $C_3N_3Cl_3$:

$$3Li_2(CN_2) + 2C_3N_3Cl_3 \rightarrow 3C_3N_4 + 6LiCl.$$

Reactions with $Li_3(BN_2)$ and $C_3N_3Cl_3$ were carried out using molar ratios of 1:1, targeting a hypothetical B–C–N-compound with the composition of BC₃N₅:

$$Li_3(BN_2) + C_3N_3Cl_3 \rightarrow BC_3N_5 + 3LiCl.$$

However, the infrared spectrum of the reaction product synthesized from $Li_3(BN_2)$ and cyanuric chloride is nearly identical to the spectra of the materials made with $Li_2(CN_2)$ or H_2NCN . Moreover, as reactions of metal chlorides and $Li_3(BN_2)$ have yielded metal nitrides and (amorphous) BN [19], it seems unlikely that the tubes from our reactions with $Li_3(BN_2)$ contain boron. It could be assumed instead, that one nitrogen atom is separated from the $(BN_2)^{3-}$ ion and contributes to the formation of the tubes whereas the remaining BN might be part of the amorphous pellet, which is found at the bottom of the reaction container:

$$Li_3(BN_2) + C_3N_3Cl_3 \rightarrow C_3N_4 + BN + 3LiCl.$$

The initial step of our reactions always seems to be the linkage of three triazine units by a nitrogen atom as evidenced by the formation of crystalline $N(C_3N_3Cl_2)_3$. When the degree of cross-linking increases at higher temperatures, the formation of the tubes is started by coating the needle-shaped crystals of $N(C_3N_3Cl_2)_3$ with a carbon nitride material. It can be concluded from the studies of the thermal behavior of $N(C_3N_3Cl_2)_3$, that the template crystals start to sublime and to decompose in the temperature region 320-400 °C, leaving behind hollow, amorphous micro- and nanotubes. The yield of tubes seems to be controlled by the number of template crystals. If the reaction mixtures are heated up to the final reaction temperature of 450–550 °C without holding the temperature at 250-350 °C for a while, no or very few tubes can be found in the product. The hexagonal profile found in some of the tubes (Figs. 2 and 3), as well as the increased chlorine content on the inside (Fig. 6) and the observed filling of some of the tubes (Figs. 4 and 5) are also regarded as strong indications for the proposed mechanism for the formation of the tubes.

4. Conclusion

Reactions of cyanuric chloride with different nitrogen containing compounds yielded tubular carbon nitride materials that cannot be dissolved in water, weak acids, or organic solvents. The materials were X-ray amorphous and also showed no crystalline behavior in electron diffraction experiments. According to our observations, a template controlled mechanism can be assumed for the formation of tubes. Needle-shaped crystals of $N(C_3N_3Cl_2)_3$ were identified as an intermediate in all our reactions. Not only the formation of the template, but also the deposition of carbon nitride on the surface of the template crystals and on the wall of the reaction container as a thin layer proceed via the gas phase. Studies of the template material revealed that it decomposes above $400 \ ^{\circ}C$, and thus, is not stable at the reaction temperatures of $450-550 \ ^{\circ}C$ used for the formation of the tubes. The thermal stabilities of our carbon nitride materials are limited to $600-650 \ ^{\circ}C$, depending on the atmosphere.

The identification of $N(C_3N_3Cl_2)_3$ and its decomposition product $C_6N_7Cl_3$ as important intermediates contributes to the enlightenment of the course of reactions between cyanuric chloride and nitrogen sources such as Li_3N or $Li_2(CN_2)$ targeting the composition C_3N_4 . The appearance of the heptazine compound $C_6N_7Cl_3$ and the triazine and heptazine characteristics found in the IR spectra of the tubes give support to the assumption that our tubular materials might consist of triazine and heptazine cores. But it is still not possible to safely assign a structure model to the resulting amorphous material and the reaction mechanism is not completely understood. Thus, further searching for other intermediates in this system seems to be a reasonable approach to a better understanding of the formation and the structures of carbon nitrides from metathesis reactions.

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