Available online at www.sciencedirect.com
ScienceDirect
Solid State Communications 141 (2007) 529–534
solid state communications
www.elsevier.com/locate/ssc

Template assisted formation of micro- and nanotubular carbon nitride materials

Sonja Tragl[a], Katharina Gibson[a], Jochen Glaser[a], Viola Duppel[b], Arndt Simon[b], H.-Jürgen Meyer[a,*]

[a] *Abteilung für Festkörperchemie und Theoretische Anorganische Chemie, Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany*
[b] *Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany*

Received 26 September 2006; accepted 6 October 2006 by A.H. MacDonald

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 $Li_2(CN_2)$ or $Li_3(BN_2)$. The intermediate formation of needle-shaped crystals of $N(C_3N_3Cl_2)_3$ 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 C_3N_4. 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.

PACS: 61.46.Fg; 68.37.Hk; 68.37.Lp; 78.30.-j; 81.16.Be

Keywords: A. Carbon nitride; A. Nano- and microtubes; B. Chemical synthesis; C. Scanning and transmission electron microscopy

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 B_4C, 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 sp^3-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-C_3N_4 are displayed in Fig. 1. The arrangement of $[N(C_3N_3)]$ and $[N(C_6N_7)]$ 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.

---

[*] Corresponding author. Fax: +49 7071 295702.
E-mail address: juergen.meyer@uni-tuebingen.de (H.-J. Meyer).

0038-1098/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2006.10.008

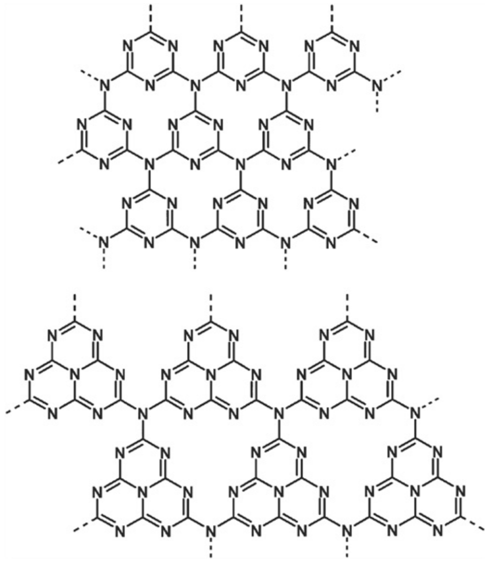

Fig. 1. Nitrogen-bridged s-triazine $[N(C_3N_3)]$ (top) and tri-s-triazine $[N(C_6N_7)]$ (bottom) units as possible building blocks of g-C_3N_4 structures.

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 $TiCl_3$, $NbCl_5$ and $NiCl_2$ 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. $Li_2(CN_2)$ was prepared from Li_2CO_3 and ammonia according to the method of Perret [20]. For the synthesis of $Li_3(BN_2)$, Li_3N and α-BN were reacted at 800 °C in sealed copper ampoules [21]. $Na_2(CN_2)$ was made from $NaHCN_2$ and $NaNH_2$ [22]. Commercially available $Na[N(CN)_2]$ (ABCR, 96%), Li_3N (Alfa Aesar, 99.5%), and H_2NCN (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 $N(C_3N_3Cl_2)_3$ [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 2-amino-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.