JOURNAL OF MATERIALS SCIENCE **40** (2005) 2645–2647 LETTERS

Turbostratic carbon nitride prepared by pyrolysis of melamine

Y. C. ZHAO, D. L. YU, H. W. ZHOU, Y. J. TIAN
Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, P.R. China
E-mail: fhcl@ysu.edu.cn

O. YANAGISAWA
Department of Mechanical Materials Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi- Hiroshima, Hiroshima 739-8527, Japan

Since the theoretical calculations predicted that the hardness of C_3N_4 covalent compound might be comparable to or even higher than that of diamond [1, 2], many attempts have been made to synthesis this novel substance. Due to the great thermodynamic stability of N_2, however, the ideal structural transition from precursor to crystalline carbon nitride is difficult to realize. In most cases, only amorphous products with low nitrogen content were obtained [3]. To solve this problem, it is good to prepare carbon nitride in graphitic or turbostratic form firstly, and then using it as precursor to synthesize other carbon nitride crystalline phases. Therefore, graphitic C_3N_4 have recently attracted more attention. Through different routes, graphitic C_3N_4 has been synthesized [4–6]. For previous work, the claimed graphitic-like C_3N_4 with unique (002) diffraction peak has the turbostratic structure actually [7–10], for the lake of other peaks in their XRD patterns. Meanwhile, the (002) spacing of those obtained turbostratic carbon nitrides are in the range of 0.32–0.33 nm.

The graphitic C_3N_4 predicted by Teter and Hemley [11] can be described as a perfect de-ammonation polycondensate of melamine, therefore, melamine was often chosen as the carbon nitride precursor to synthesize graphitic C_3N_4 by electrodeposition [6] and solvothermal method [7]. Pyrolysis of melamine was investigated [12] in 1988, however, the authors focused their attention only on its thermal behavior, and they didn't consider the possibility as potential candidate for carbon nitrides after complete polycondensate. Recently, pyrolysis of melamine under high pressure was studied at the temperatures up to 700 °C [13]. Obvious nitrogen loss made the attempt unsuccessful. In this letter, we report an improved pyrolysis route to prepare turbostratic carbon nitride from melamine.

The pyrolysis was performed in two steps: first, the temperature was maintained at 300 °C in order to realize the primary condensation (melamine → melam) as complete as possible; and then it was risen to 650 °C to perform the advanced condensation. In the experimental, melamine was pyrolyzed in a quartz tube with a diameter of 35 mm, and an outer-thimble-shape heater was used. Melamine was placed at the middle of the quartz tube. The pyrolysis was conducted at 300 °C for 1 hr, then at 600° for 2 hr in atmosphere; after milling, the obtained powder was maintained at 300 °C for 0.5 hr, then at 650 °C for 1 hr in vacuum. Finally, a kind of brown carbon nitride powder was obtained.

The chemical composition was analyzed by using elemental analyzer (LECO, CHN-1000) and EDX (EDAX INC., Phoenix). The product was characterized by X-ray diffraction (XRD) with Cu-Kα radiation (JEOL, ROTEX JRX-12), fourier transfer infrared (FTIR) spectroscopy (Bruker, EQUINOX55), scanning electron microscopy (SEM) (TOPCON, SM-520), and transmission electron microscopy (TEM) coupled with selected area diffraction (SAED) (JEOL, JEM-2010) and thermogravimetry (TG) (NETZSCH, STA449C/6/G).

The composition of the product characterized by elemental analysis and EDX is listed in Table I. SEM observation found that the particles dimension ranged from 5 μm to 20 μm. Most of the particles show the flake-like morphology. Fig. 1 shows a typical XRD pattern of the product. There is a single main peak at the position of 27.62°, which suggests that the product was turbostratic. Its corresponding d-spacing is 0.321 nm similar to the (002) plane of the turbostratic/graphite-like carbon nitrides obtained in previous work [9, 14].

The FTIR spectrum of the prepared turbostratic carbon nitride and melamine are shown in Fig. 2. The IR spectrum of melamine presents three absorption bonds: 3000–3650 cm^{-1}, 1100–1700 cm^{-1}, and the last one centered at about 810 cm^{-1}. The 3000–3650 cm^{-1} band is assigned to N—H stretching vibration modes, the 1100–1650 cm^{-1} band corresponds to the stretching vibrations related to C—N, C=N, and is generally associated with the skeletal stretching vibrations of these aromatic rings. The absorption at 810 cm^{-1} is characteristic of out-of-plane bending modes of these rings. The 460–850 cm^{-1} band is linked to the C—NH_2 group and the ring breadth or bending vibration modes [15]. Comparing the FTIR spectrum of the turbostratic carbon nitride with that of melamine, it reveals that after pyrolysis, the previous strong absorption peaks in the range of 3000–3650 cm^{-1} have disappeared, only a board absorption bond is left, which suggest that most of the N—H bonds have been destroyed during the de-ammonation condensation. While the increased number of absorption peaks ranging from 1100 to 1700 cm^{-1} implies the condensation of 1,3,5-s-triazine rings making the related chemi-

0022–2461

TABLE I Composition of the obtained product

	C (at%)	N (at%)	H (at%)	O (at%)	C/N
Elemental analysis	32.47	50.14	17.39		0.648
EDX	38.89	59.60		1.50	0.653

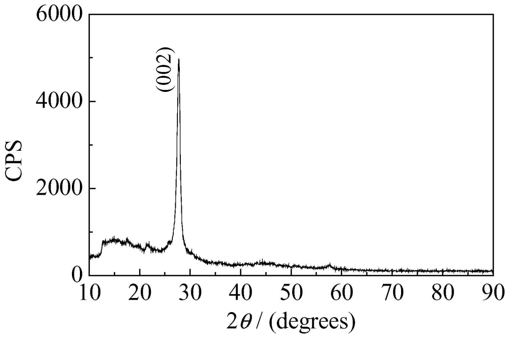

Figure 1 XRD pattern of the obtained product.

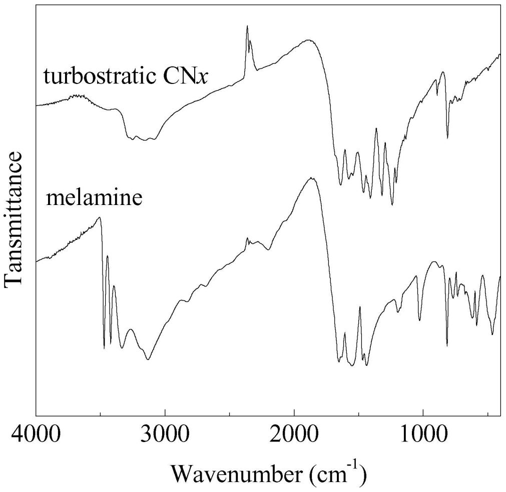

Figure 2 FTIR spectrum of the obtained product and melamine.

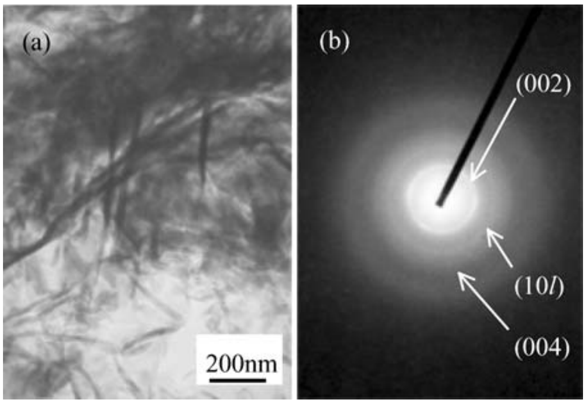

Figure 3 (a) TEM image of flake-like turbostratic carbon nitride and (b) corresponding SAED pattern.

cal environment complicated. The peak at 2360 cm^{-1} is attributed to the environmental CO_2 background inside the spectrometer.

TEM observations coupled with SAED are performed. As shown in Fig. 3a, most of the particles are present in the form of flake-like, which is consistent with the SEM results. In addition, it is interesting that some nanowires can be obviously observed. The nanowires have the width of about 30 nm and the length of from 200 nm to 1000 nm. Fig. 3b shows the corresponding SAED pattern. Three board diffraction rings match (002), (10*l*) and (004) planes of the turbostratic structure, respectively. Moreover, the (002) plane with *d*-spacing of 0.32 nm is similar to that from the XRD results. Outside the (004) diffraction ring, there also exists an amorphous ring. Some particles with strip-like morphology were also observed. The typical bright-filled TEM image and its corresponding SAED pattern are shown in Fig. 4a and b, respectively. It is novel that large numbers of continuous nanowires are embodied in the trip-like particles, whose width is also about 30 nm, same as that of the nanowires observed in the flake-like particles (Fig. 3a). Fig. 4b shows strip-like particles have the same turbostratic structure. However, the diffraction rings become sharper obviously, which indicates that they have higher structural order. In the direction marked by the arrows, the brightness of (002) diffraction ring is higher than that in other directions, which suggest that the arrangement of the nanowires leads to a preferential orientation. During the pyrolysis of melamine, both cyclic and linear branching condensations can realize through —NH bridges [16]. The former condensate acts as the basic unit to build the turbostratic structure, therefore the flake-like particles form easily. The latter could result in the formation of the observed nanowires.

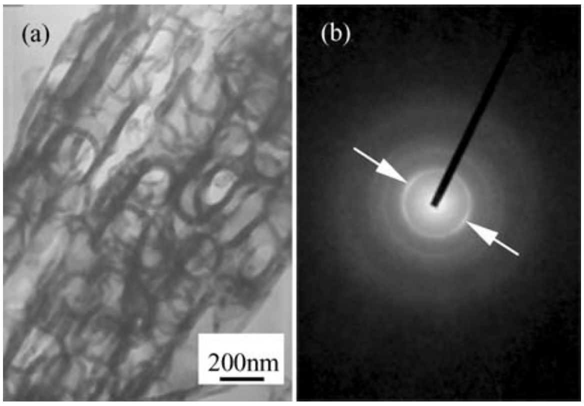

Figure 4 (a) TEM image of strip-like turbostratic carbon nitride and (b) corresponding SAED pattern.

The thermogravimetric analysis (TG) of the pyrolytic product was performed under argon flux. The TG curve is given in Fig. 5. A unique inflexion point appears at 720 °C, and then the product decomposed drastically. The absence of the inflexion point at about 380 °C indicates that no NH_3 is eliminated [7, 12]. The total mass loss is close to 100%, there is only a little of black residue left, which imply that most of the product is evaporated with the formation of HCN and N_2. The product keeps its thermal stability up to 700 °C, which is higher than that of melamine.

In summary, a kind of turbostratic carbon nitride was obtained through de-ammonation polycondensation of melamine. Turbostratic carbon nitride nanowires originating from the linear branching condensations in the

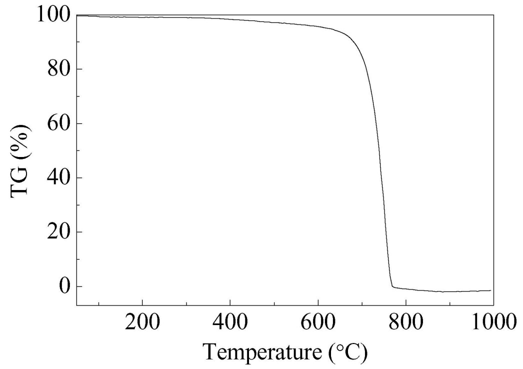

Figure 5 TG curves of the obtained product.

product were observed. The pyrolytic product with the C/N atomic ratio of 1:1.65 and higher thermal stability should be a good precursor for the high-temperature and high-pressure synthesis of carbon nitride crystals.

Acknowledgments

This work was supported by National Natural Science Foundation of China (Grant No. 50225207, 50342033 and 50372055) and Natural Science Foundation of Hebei Province, China.

References

1. A. Y. LIU and M. L. COHEN, *Science* **245** (1989) 841.
2. A. Y. LIU and R. M. WENTZCOVITCH, *Phys. Rev. B* **49** (1994) 5034.
3. THOMAS MALKOW, *Mater. Sci. Eng. A* **302** (2001) 311.
4. D. L. YU, F. R. XIAO, T. S. WANG, Y. J. TIAN, J. L. HE, D. C. LI and W. K. WANG, *J. Mater. Sci. Lett.* **19** (2000) 553.
5. Y. J. BAI, B. LU and Z. G. LIU, *J. Cryst. Growth* **247** (2003) 505.
6. CHAO LI, CHUAN-BAO CAO and HE-SUN ZHU, *Mater. Lett.* **58** (2004) 1903.
7. H. MONTIGAUD, B. TAMGUY, G. DEMAZEAU, I. ALVES and S. COURJAULT, *J. Mater. Sci.* **35** (2000) 2547.
8. ALEXEY ANDREYEV, MINORU AKAISHI and DMITRI GOLBERG, *Chem. Phys. Lett.* **372** (2003) 635.
9. QIXUN GUO, YI XIE, XINJUN WANG, SHICHANG LV, TAO HOU and XIANMING LIU, *ibid.* **380** (2003) 84.
10. TAMIKUNI KOMATSU and TAKAKO NAKAMURA, *J. Mater. Chem.* **11** (2001) 474.
11. D. M. TETER and R. J. HEMLEY, *Science* **271** (1996) 53.
12. L. COSTA and G. CAMINO, *J. Therm. Anal.* **34** (1988) 423.
13. H. A. MA, X. P. JIA, L. X. CHEN, P. W. ZHU, W. L. GUO, X. B. GUO, Y. D. WANG, S. Q. LI, G. T. ZOU, GRACE ZHANG and PHILLIP BEX, *J. Phys.: Condens. Matter* **14** (2002) 11269.
14. TAMIKUNI KOMATSU, *J. Mater. Chem.* **11** (2001) 799.
15. M. K. MARECHEWKA, *Mater. Sci. Eng. B* **95** (2002) 214.
16. C. DEVALLENCOURT, J. M. SAITER, A. FAFET and E. UBRICH, *Therm. Acta* **259** (1995) 143.

Received 29 July
and accepted 27 October 2004