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Synthesis of beta carbon nitride nanosized crystal through mechanochemical reaction

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Abstract
Nanosized beta carbon nitride (β-C_3N_4), of grain size several tens of nanometres, has been synthesized by mechanochemical reaction processing. The low-cost synthetic method developed facilitates the novel and effective synthesis of nanosized crystalline β-C_3N_4 ($a = 6.36$ Å, $c = 4.648$ Å) powders. The graphite powders were first milled to a nanoscale state, then the nanosized graphite powders were milled in an atmosphere of NH_3 gas. It was found that nanosized β-C_3N_4 was formed after high-energy ball milling under an NH_3 atmosphere. After thermal annealing, the shape of the β-C_3N_4 changes from flake-like to sphere-like. The nanosized β-C_3N_4 formed was characterized by x-ray diffraction, Fourier transformation infrared spectroscopy, and transmission electron microscopy. A solid–gas reaction mechanism was proposed for the formation of nanosized β-C_3N_4 at room temperature induced by mechanochemical activation.

The preparation of binary, ternary, or quaternary materials from light elements (B, C, N, . . .) is of considerable current interest. The most exciting material in this family is the carbon nitride C_3N_4, for which a hardness challenging that of diamond is predicted. Since Cohen emphasized that the bulk-modulus value for C_3N_4 would be close to or higher than that of diamond (442 GPa) or c-BN (369 GPa) [1], the C_3N_4 phases have attracted much interest because of their potential application in the field of low-compressibility materials [2–4]. Synthesis routes suggested for carbon nitride compounds include shock-wave compression technology [5], pyrolysis of high-nitrogen-content precursors [6], diode sputtering [7], pulsed laser ablation [8], and ion implantation [9]. Experimental studies, mostly on thin films, show

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that nanometre sized crystals usually embed in amorphous matrix [7, 8, 10–12]. In several cases, crystallites with a tetragonal structure [3] and even a monoclinic phase [12] have been reported recently. The defect zinc-blende structure also appears to form when using a chemical precursor technology [13].

X-ray powder diffraction or selected-area electron diffraction (SAED) in single-crystal studies of the carbon nitrides could provide definitive structural information. Serious doubts that these potentially superhard materials have actually been made will remain until large crystals of carbide are synthesized and precisely characterized and their mechanical properties tested. In summary, it has been suggested, on the basis of the large amount of experimental results available so far, that physical deposition methods are unable to yield the crystalline hard material [14–16].

The difficulties in the synthesis of hard carbon nitrides are very probably related to their low thermodynamic stability with respect to the elements (C and N_2), indicated by a positive value of the enthalpies of formation [17]. Nguyen and Jeanloz [18] described the first example of a dense carbon nitride formed in the bulk, synthesized at high pressure and high temperature. The synthesis at HPHT may offer a more promising route to achieving this goal [19]. Despite recent advances, commercial exploitation of nanopowders is currently limited by the high synthesis cost. McCormick [20] and Hu *et al* [21] suggest that solid-state displacement reaction induced by a mechanical milling process can be employed to induce a high-pressure synthesized phase. To our knowledge, only one paper related to CN_x produced by mechanochemical processing in an atmosphere of N_2 gas has appeared [22]. In the present paper, direct evidence has been obtained from x-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transformation infrared spectroscopy (FTIR) that nanosized carbon nitride powders of β-C_3N_4 can be synthesized in the form of bulk under conditions of high-energy ball milling in an atmosphere of NH_3 gas. A possible mechanism for the nanosized β-C_3N_4 formation has been proposed.

The ball-milling experiments were performed in a conventional planetary ball miller at room temperature using hardened steel balls with a diameter of 25 mm and a stainless steel cell. Graphite powders with a high purity of 99.99% were used. The cell was loaded with 10 g of the graphite powders together with several balls. The graphite powders were first milled to a nanoscale state under argon atmosphere at 600 rpm for 40 h, and then the cell was purged with the NH_3 reaction gas several times and a starting pressure of 300 kPa was established prior to milling; after that, the previously milled graphite powders were milled for about 60 h under an NH_3 atmosphere. Thermal annealing experiments were performed at 680 and 750 °C under a flow of N_2. The powders were characterized by means of XRD with Cu Kα radiation and FTIR. Investigations of the morphology and crystal structure of the particles formed were also performed on a TEM coupled with SAED.

In TEM, the graphite powders milled for 40 h in an atmosphere of argon are several tens of nanometres in grain size; most of the graphite is in an amorphous state. On the evolution of graphite under high-energy ball milling, there have been several papers published recently [23, 24]. After 60 h of high-energy ball milling under an NH_3 atmosphere, it was found that the carbon nitride compound has been formed. Figure 1 shows an XRD pattern of the β-C_3N_4 powder. The 200, 210, 300, 220, 301, 320, 102, 112, and 202 peaks in the XRD spectrum in figure 1 match well with the calculated values of the d-spacing of β-C_3N_4 of 2.772, 2.095, 1.848, 1.600, 1.465, 1.272, 1.175, 1.125, and 1.103 Å, respectively. Because the grain size of the formed β-C_3N_4 is usually several tens of nanometres, the XRD peaks are wider while the intensity of the peaks is low. The bonding state of C–N can be revealed by FTIR spectroscopy [25, 26]. Figure 2 shows a typical FTIR spectrum. The peaks at 1008 and 1380 cm^{-1} correspond to C–N stretching bonds. No peaks corresponding to C=N bonds
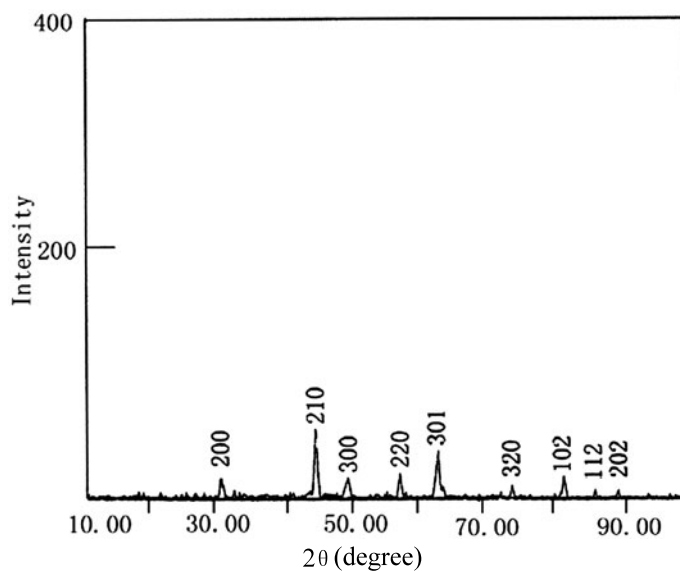
Figure 1. An XRD pattern for beta carbon nitride (β-C_3N_4) powders synthesized by high-energy ball milling under an NH_3 atmosphere.
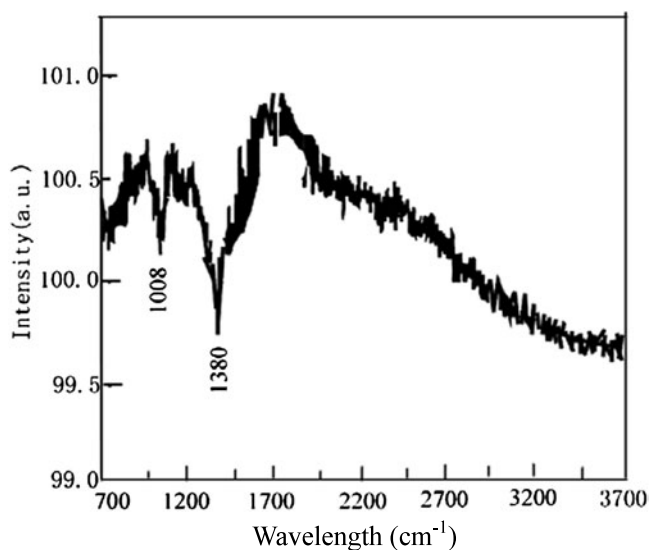

Figure 2. An FTIR spectrum of β-C_3N_4 powder.

were found in the FTIR spectrum. This suggests the formation of crystalline β-C_3N_4 and is in accordance with the result obtained from XRD.

Figure 3(a) illustrates a typical TEM image of the β-C_3N_4 phase obtained directly by mechanochemical processing, which has not been treated by thermal annealing. The β-C_3N_4 phases are about one to several tens of nanometres in dimensions, and they are present in a flake-like form. From SAED patterns shown in figure 2(b), a polycrystalline β-C_3N_4 phase with a lattice constant of $a = 6.36$ Å, $c = 4.648$ Å can be determined. In the SAED pattern
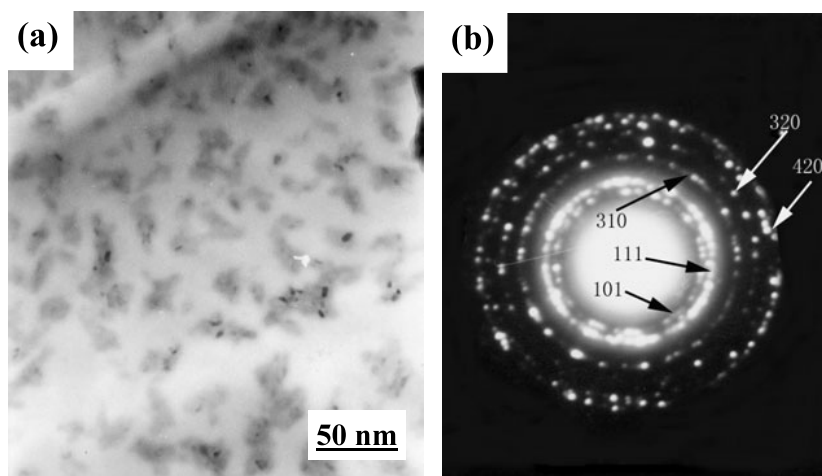
Figure 3. (a) A TEM image of ultrafine flake-like β-C_3N_4 powders prepared by mechanochemical processing under an NH_3 atmosphere. (b) The corresponding SAED pattern suggests that the phases in figure 2(a) are β-C_3N_4; the (101), (111), (310), (320), and (420) diffraction rings correspond well to d-spacings of β-C_3N_4 of 2.206, 1.922, 1.538, 1.272, and 1.048 Å, respectively.

of figure 2(b), the (101), (111), (310), (320), and (420) diffraction rings correspond well to d-spacings of β-C_3N_4 of 2.206, 1.922, 1.538, 1.272, and 1.048 Å, respectively.

After thermal annealing, the morphology of the β-C_3N_4 transforms from flake-like to sphere-like. We now consider the thermally annealed β-C_3N_4 powders: unlike the SAED pattern for β-C_3N_4 powders not treated by thermal annealing, the single-crystal SAED patterns of the β-C_3N_4 phase from different zone axes can be easily obtained. Figures 4(a) and (c) show two typical TEM images of β-C_3N_4 samples, which have been isothermally treated at 680 and 720 °C under N_2 atmospheres for 3 h, respectively. It was found that the grain size of the β-C_3N_4 becomes larger than that of figure 2, and the colour of the nanoscaled particles becomes deeper. Figures 4(b) and (d) demonstrate two SAED patterns corresponding to figures 4(a) and (c), respectively. The β-C_3N_4 phase can be identified from the [123] zone axis in figure 4(b) and the [212] zone axis in figure 4(d).

The formation of the nanosized β-C_3N_4 has shown a solid–gas reaction mechanism induced by mechanical reaction. During milling, fracture and welding of reactant graphite powder particles occur repeatedly during ball/powder collision events. Plastic deformation of the graphite powder particles initially occurs by the development of shear bands, and the graphite particles decompose into sub-grains separated by low-angle grain boundaries. With further milling, the size of the sub-grain decreases and nanometre size sub-grains form. Because the nanosized powders can exhibit properties that substantially differ from those of bulk materials as a result of particle dimension, surface area, quantum confinement, and other effects, it is easy for the nanosized graphite to react with the nitrogen of NH_3. In the meantime, high pressure occurs as ball/powder collisions take place repeatedly; thus the mechanical milling technique can be employed to induce a high-pressure phase. So a ball mill can be considered to be a chemical reactor in which a wide range of chemical reactions can take place under high temperature and high pressure [20, 21]. In the present paper, during the mechanochemical processing under NH_3 atmospheres, as the nanosized graphite powders formed, the nanosized graphite powders tended to react with the nitrogen atoms in NH_3. Mechanochemical synthesis for β-C_3N_4 powders provides an effective and low-cost
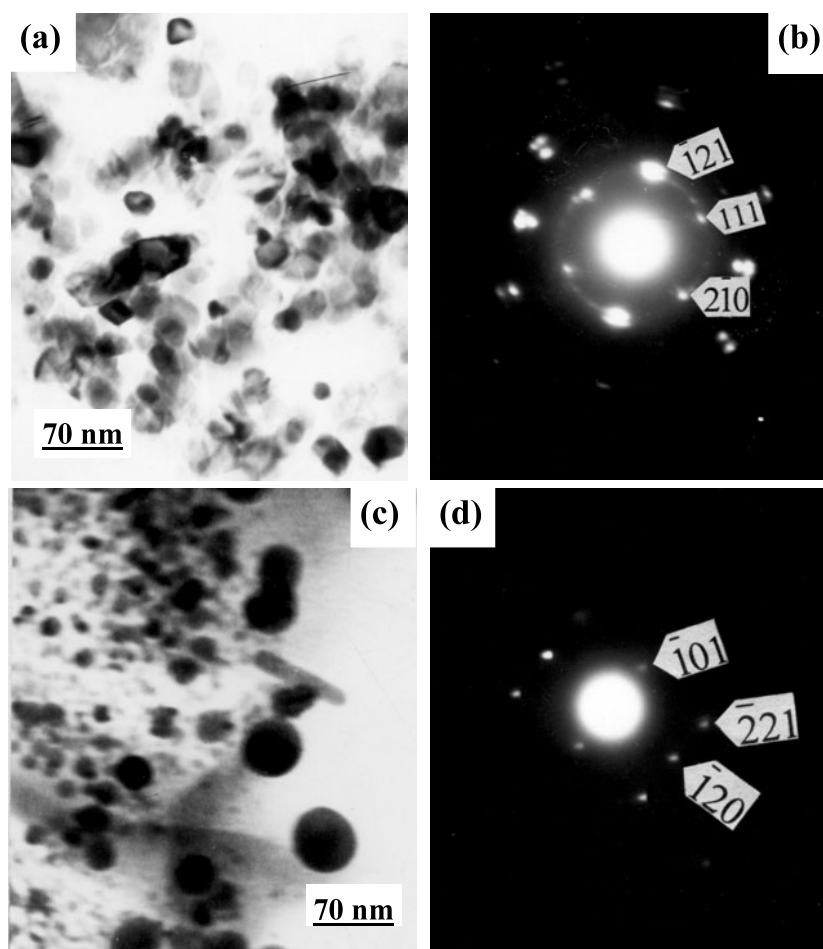
Figure 4. (a) A TEM image of sphere-like β-C_3N_4 particles after thermal annealing at 680 °C for 3 h in an atmosphere of N_2 gas. (b) The corresponding SAED pattern from the [123] zone axis indicates that the nanoscaled phase in (a) is β-C_3N_4 with lattice constants of $a = 6.36$ Å, $c = 4.648$ Å. (c) A TEM image of sphere-like β-C_3N_4 particles after thermal annealing at 720 °C for 3 h in an atmosphere of N_2 gas. (d) The corresponding SAED pattern from the [212] zone axis indicates the β-C_3N_4.

method for the preparation of ultrahard carbon nitride. Unlike previously reported results on carbon nitrides, the present result should not suffer from obscuring signals from the amorphous matrix or the substrate and can provide direct and precise information about the carbon nitride compounds.

In conclusion, this study facilitates the novel and effective synthesis of nanosized beta carbon nitride powders by a low-cost synthesis method developed here. The graphite powders were first milled to a nanoscale state, then the nanosized graphite powders were treated in an atmosphere of NH_3 gas through a mechanochemical reaction. It was found that nanosized beta carbon nitride (β-C_3N_4) with a grain size of several tens of nanometres has been formed by mechanochemical processing. After thermal annealing, the β-C_3N_4 shape changes from flake-like to sphere-like. The nanosized β-C_3N_4 formed was characterized by means of XRD and TEM. In the FTIR spectrum, the peaks at 1008 and 1380 cm^{-1} revealed the C–N stretching

bonds of the carbon nitride. A solid–gas reaction mechanism was proposed for the nanosized β-C$_3$N$_4$ formation at room temperature induced by mechanochemical activation.

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