

Synthesis of C-BN hybride nano structures

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This study reports on the mechano-thermal synthesis of carbon – boron nitride nano structures from elemental graphite and boron nitride powders. Initially, amorphous hybrid structure was obtained by high energy ball milling technique from hexagonal graphite and hexagonal boron nitride powders. X-ray spectra taken from ball milled samples indicated that the hexagonal graphite and boron nitride, composed of layers, was transformed into the amorphous hybrid for a milling time of 20 h by the way of high energy input. Subsequent isothermal annealing of milled hybrid powders was conducted at 1300 °C for 2 h in Ar gas. It was revealed via investigation of transmission electron microscopy that carbon – boron nitride hybrid nano structures were formed after annealing.

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1. Introduction

After the Carbon Nanotube (CNT) was discovered in 1991, scientists have started to investigate other materials which have the same tube structure [1]. Boron Nitride Nanotubes (BNNT) is one of these materials. Theoretically, BNNT was discovered by Rubio in 1994 and was successfully synthesized by Chopra in Berkeley University in 1995 [2-4]. And then, BNNTs were synthesized by different methods [5-6]. BNNTs are a new alternative of CNTs which have been frequently used in different fields recently. The cubic and hexagonal phases of BN show mechanical and thermal properties that are very similar to those of diamond and graphite, respectively. However, in contrast to carbon nanofibers and carbon nanotubes (CNTs), BN nanostructures are electrically insulating, with an energy gap of ~5.5 eV [7-9] and resistant to oxidation up to 800 °C [10].

Hybrid structures of boron nitride nanotubes (BNNTs) and carbon nanotubes (CNTs) are expected to have appealing new properties that are not available from pure BNNTs and CNTs. Theoretical studies indicate that BNNT/CNT junctions could be multifunctional and applicable as memory, spintronic, electronic, and photonics devices with tunable band structures [11].

In this study, the synthesis of carbon – boron nitride hybrid nanostructures was performed by using the mechano-thermal method. After high-energy ball milling process, powders were annealed at high temperature. Ball milling and thermal annealing caused nucleation and grown of hybrid nanotubes and hybrid nano-structures at different forms.

2. Experimental method

Commercial hexagonal graphite powders (Merck kGAA, 99.5%) and Boron Nitride (h-BN) powders (Merck kGAA, 99%) was used as starting materials. Hexagonal graphite powders and hexagonal boron nitride powder mixture was milled in a high energy ball milling. Equipment that the, Retsch PM 200, was used with the rotational speed of the vial at 500 rpm. Hardened steel vials containing 1 g graphite and 1 g boron nitride powders were used. The ball milling was carried out 8 mm balls (100Cr4) and ball-to-powder weight ratio (BPR) 15:1. Iron powder was added as a catalyst for formation of nanotubes of 2 at. % ratio. Milling process were performed in inert atmosphere in order to prevent oxidation. Inert atmosphere was 99.9 % Argon. Graphite and boron nitride powder mixture were dry milled for 20h under condition of 30 min process and 10 min duration for cooling. The milled samples were annealed in the alumina-tube furnace under Ar gas flow (about 3×10^{-2} l/min) at 1300 °C for 2h. The structural characterizations of the milled samples were investigated by using Bruker X-ray diffractometer (XRD) with CuK α radiation. The microstructure of the milled and annealed samples were investigated by high-resolution transmission electron microscope (HRTEM) (JEOL Jem 2100F), Scanning Electron microscope (SEM) (Jeol Jsm-7001F). Chemical composition was examined using X-ray energy dispersive spectrometer (EDX) equipped with an Oxford Isis EDX system.

3. Results and discussions

Nanotube structures couldn't produced by direct heating of the graphite and boron nitride powders without any mechanical or chemical treatment because both graphite and hexagonal boron nitride are very stable. To

provide the different structures formation of graphite and boron nitride (such as nano onion, nanotube), high temperature (above 3000 °C) was required or covalent bonds within the graphite must be deformed by the other methods. The role of ball milling treatment is to create precursor containing nucleation structures and free carbons atoms as mechanical treatment [4,12,13].

The characteristic (002) peaks exist in XRD spectras of both hexagonal graphite and hexagonal boron nitride (Fig 1a and b). After 5-hour milling process, these peaks disappeared completely; in other words, the structure was completely amorphized (Fig 1c).

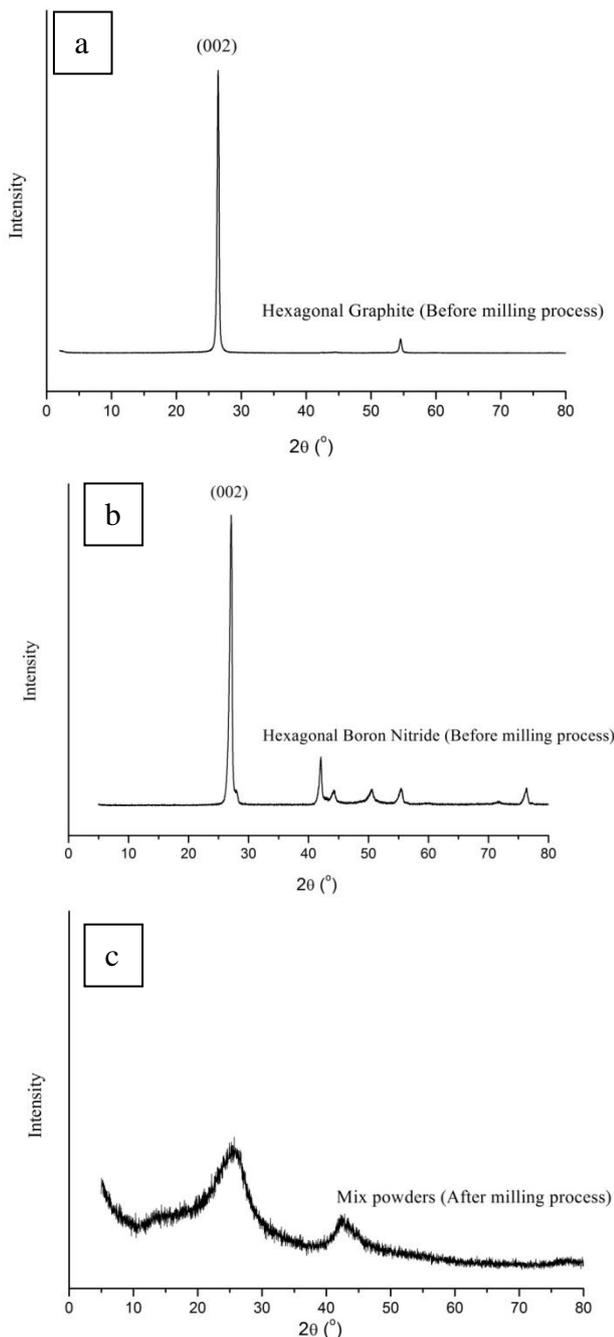


Fig. 1. XRD spectras of a) hexagonal graphite b) hexagonal boron nitride c) mix powder after 5-hour milling process.

Fig. 2 shows TEM image of milled sample before annealing process. The Structure is composed of amorphous carbon-boron nitride mixture and nano porous particles. In Fig. 2.a, it is seen that the disordered of graphite and boron nitride sheets and particle mixtures (Fig. 2.a.). We thought before TEM investigation that amorphous structures would be seen during TEM investigation of milled sample (without annealing). But, we observed nanotubes were surprisingly formed during ball milling process (Fig. 2.b). The walls of formed nanotubes are not smooth and contain too much defect. We think that these nanotubes formed with the aid of high temperature which was caused by collisions of balls during milling. These tubes can be identified by “hemi-nanotubes”

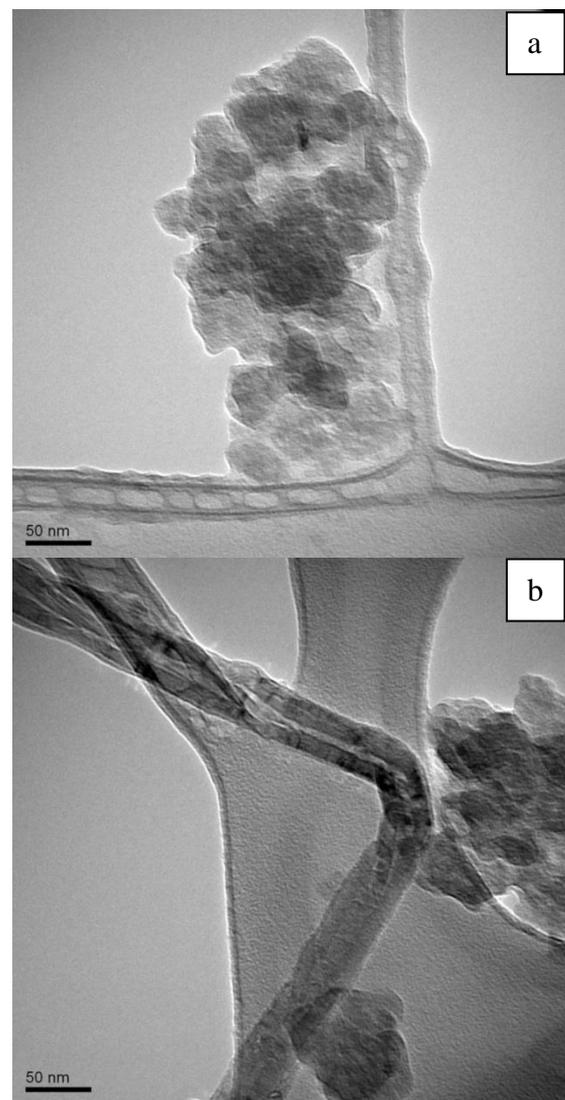


Fig 2.a,b; TEM image of milled carbon-boron nitride a) nano particle and C-BN sheets mixture b) Thick complex nanotube at the “V” shape

The SEM and TEM images in Fig. 3 show structures in carbon-boron nitride powder mixture which milled and then annealed at 1300 °C for 2 h. The SEM image show the spherical nano structures and these structures are intensive in the sample (Fig. 3.a.). The TEM images (Fig.

3b) reveal that the carbon-BN powder mixture consists of quasispherical nanoparticles, with diameters ranging between 20 and 50 nm. These quasispherical structures are nano-porous. They aren't shown before annealing process but after heat treatment these structures are observed.

Carbon and nitrogen peaks in EDX analysis are weak compared to boron peak. So, we think that a reaction may occur between carbon and nitrogen atoms by effect of high temperature. And also, the reason of porosity in structure may be cause of this reaction.

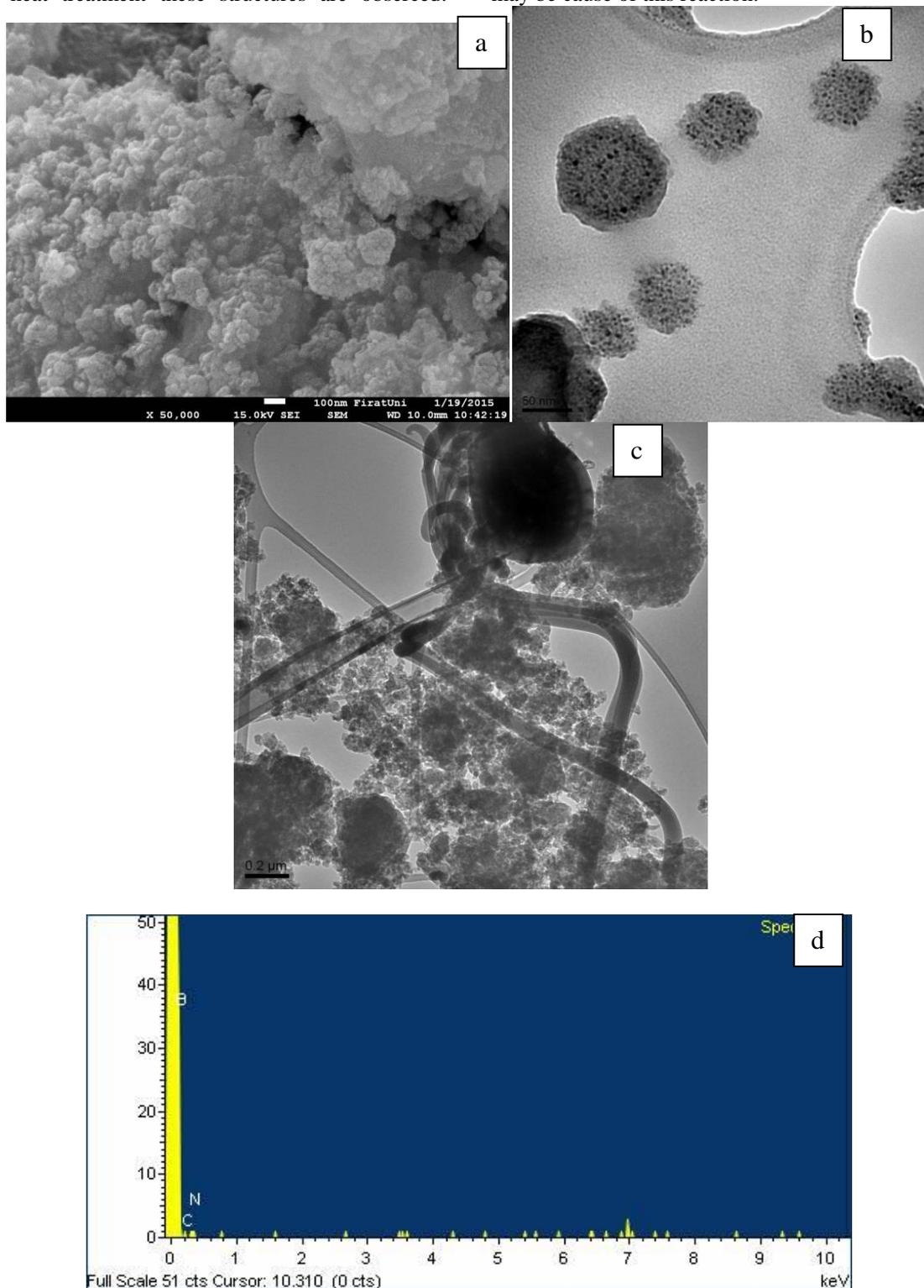


Fig. 3. TEM and EDX images of milled (20h) and then annealed (1300 °C for 2 h) sample

Fig.3.c and d show TEM and EDX images of milled (20h) and then annealed (1300 °C for 2 h) sample. It was seen that nanotubes were formed after mechano-thermal process. EDX analysis of nanotubes consists of boron, nitrogen and carbon atoms. This nanotube structure can be described as hetero-junction nanotube [12]. In annealed sample, nanotubes amount was limited. But, formed nanotubes were very smooth compared to milled sample (without annealing). It is thought to be that by this way smooth nanotubes were observed. Annealing temperature causes the disappear of defects on nanotubes walls in milled sample

Some theoretical studies show that BNNT/CNT junctions and h-BN/graphite sheets are very stable [14-17], Calculations have shown that the energy required for a N atom (or B atom) to exchange with a C atom at a BNNT/CNT junction is rather large (2.1 and 2.0 eV, respectively). Ball milling process provides homogenous distribution of B, N and C atoms in a tube or other hybrid structures. During milling process, hexagonal boron nitride and graphite powders were amorphized and also B, N and carbon atoms were solute in the iron particles. As catalyst, we think that the iron particles became saturated by B, C, N due to the B, C, N solubility limit. In the iron, the diffusion process of the B, C, N in the iron particles occurred during the annealing process and these atoms were re-arranged as tubular. In addition, nano-porous structures occur in powder samples because of partial reactions and also these particles couldn't change to tubular structures which served as catalyst.

4. Conclusion

The hexagonal graphite and boron nitride, composed of layers, was transformed into the amorphous hybrid for a milling time of 20 h and subsequent isothermal annealing of milled hybrid powders was conducted at 1300 °C. Carbon-BN powder mixture consists of quasispherical nanoparticles, with diameters ranging between 20 and 50 nm. In addition, smooth nanotubes were formed after mechano-thermal process. Even, nanotubes were also formed during ball milling. But, they consist of many defect in their walls. Although aim of this study was production of C-BN hybrid nanotubes, different structures also formed. Our studies continue to increase hybrid nanotube amount and to understand formation mechanism.

References

- [1] S. Iijima, *Nature*, **354**, 56 (1991).
- [2] A. Rubio, J.L. Corkill, M.L. Cohen, *Phys. Rev.*, **B49**, 5081 (1994).
- [3] N.G. Chopra, R.J. Luyken, K. Cherrey V.H. Crespi, M.L. Cohen, S.G. Louie, A. Zettl, *Science* **269**, 966 (1995).
- [4] C.C. Tang, X.X. Ding, X.T. Huang, Z.W. Gan, S.R. Qi, W. Liu, S.S. Fan., *Chemical Physics Letters*, **356**, 254 (2002).
- [5] S. H. Güler, M. Aksoy, E.Evin, Ö. Güler, *J. Optoelectron. Adv. Mater.* **16**(7-8), 831 (2014).
- [6] T. Lauda, *Boron Nitride Nanotubes Grown By non-Ablative Laser Heating: Synthesis, Characterization, Growth Processes*, Phd, University Of Tsukuba, Japan, 2001.
- [7] M.-F. Ng and R. Q. Zhang, *Physical Review B*, **69**(11), Article ID 1154176, 6 pages, 2004.
- [8] G. G. Fuentes, E. Borowiak-Palen, T. Pichler, et al., *Physical Review B*, **67**(3), Article ID 035429, 6 pages, 2003.
- [9] W.-Q.Han, W. Mickelson, J. Cumings, A. Zettl, *Applied Physics Letters*, **81**(6), 1110 (2002).
- [10] L. A. Chernozatonskii, E. G. Gal'pern, I. V. Stankevich, and Y. K. Shimkus, *Carbon*, **37**(1), 117 (1999).
- [11] K. C. Lau, Y. K. Yap, R. Pandey, *B-C-N Nanotubes and Related Nanostructures Lecture Notes in Nanoscale Science and Technology* **6**, 271 (2009).
- [12] S.A. Maksimenko, V.N. Rodionova, G.Y. Slepyan, et al., *Attenuation of electromagnetic waves in onion-like carbon composites*, *Diamond Relat. Mater.* **16**(4-7), 1231 (2007).
- [13] Ö. Güler, E. Evin, *Formation of Carbon Nano Onions by Thermo-Mechanical Processing of Graphite Powders*, *Materials Testing*, **56**(3), 241 (2014).
- [14] X. Blase, J.C. Charlier, A. DeVita, R. Car, *Appl Phys Lett*, **70**, 197 (1997).
- [15] S. Okada, M. Igami, K. Nakada, A. Oshiyama, *Phys Rev B*, **62**, 9896 (2000).
- [16] S. Okada, A. Oshiyama, *Phys Rev Lett*, **87**, 146803 (2001).
- [17] J. Choi, Y.H. Kim, K.J. Chang, D. Tomanek *Phys Rev B*, **67**, 125421 (2003).