

Boron Carbide Nanowires from Castor Oil for Optronic Applications: A Low-Temperature Greener Approach

H. V. Saritha Devi

University of Kerala

M. S. Swapna

University of Kerala

S SANKARARAMAN (✉ drssraman@gmail.com)

University of Kerala

Research Article

Keywords: boron carbide, nanowires, condensation method, castor oil

Posted Date: August 18th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-60234/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

The development of one-dimensional nanostructures has revolutionized electronic and photonic industries because of their unique properties. The present paper reports the low-temperature green synthesis of boron carbide nanowires, of diameter 14 nm and length 750 nm, by the condensation method using castor oil as the carbon precursor. The nanowires synthesized exhibit beaded chain morphology, and bandgap energy of 2.08 eV revealed through the Tauc plot analysis. The structure of boron carbide nanowires is revealed by Fourier transform infrared spectroscopy and X-ray diffraction analyses. The photoluminescence study reveals the nanowire's blue light emission capability under ultraviolet excitation, which is substantiated by the CIE plot suggesting its potential in photonic applications.

1 Introduction

Nanoscale materials have received considerable attention employing their unique properties and a wide range of applications relative to their bulk counterparts [1, 2]. Nanomaterials can be classified into zero-, one-, and two- dimensional structures depending on the shape and size. Among the one dimensional (1D) nanostructures, nanowires play a significant role in device fabrication [3–5]. The properties of the nanomaterials are strongly influenced by their size, shape, and morphology. The diameter (< 10 nm) of the nanowires (NWs) introduces quantum-confined size effects, modifying the structural, electronic, optical, thermal, and magnetic properties. This enables its use in micro and nanoelectromechanical systems, sensors, and photodetectors [1, 6–9]. The wide bandgap exhibited by NWs makes it suitable for applications in light-emitting diodes, photovoltaics, and nanoscale lasers [1, 10]. NWs having high-temperature stability and high-frequency performance are essential in the development of electronic and optoelectronic systems.

Of different materials - metals, polymers, semiconductors, insulators, and ceramics - NWs of ceramic materials have gained attention recently due to their characteristic properties and widespread applications in the area of magnetic nanocomposites, quantum electronic materials, gas separations, and structural reinforcements. Ceramic materials are high strength materials and are chemically and thermally stable. Among ceramic materials, boron carbide (BC) finds widespread applications - lightweight armors, blast nozzles, ceramic bearing, brake linings, cutting tools, rocket propellant in the aerospace industry, and neutron absorber and shielding material in the nuclear industry [11–14] - due to its unique properties - greater hardness, high thermal and chemical stability, high neutron absorption cross-section, corrosion resistivity, and high melting point [15–17]. The lower fracture toughness of bulk BC is overcome by the 1D BC nanostructures having high elastic modulus [18]. The enhanced physical and electrical properties of BC NWs are responsible for the high temperature and power applications. The field emission properties of BC NWs make them a potential candidate as cathode materials [19, 20].

The performance of 1D BC nanostructures is greatly influenced by the synthesis condition [21]. Several methods, such as template-based synthesis, microwave radiation, chemical vapor deposition, and

synthesis using polymer precursors, are available to produce different morphological structures of BC [22–28]. Zhang et al. [29] synthesized BC nanowires using a plasma-enhanced chemical vapor deposition method, and high pure BC NWs are prepared by Ma et al. using the thermal evaporation method [30]. Most of these methods need pre-process conditions such as catalyst preparation, substrate, and template preparation. Despite these methods, a more convenient low-temperature method for producing BC NWs has high demand and interest.

The condensation method is one of the low-temperature synthesis methods used for BC's production using inexpensive organic precursors such as glycerin, citric acid, and polyvinyl alcohol (PVA) [31–33]. The usage of polymeric precursors enables control over the final product's properties and structures by varying the precursor composition at low-temperatures [11, 34, 35]. Based on the above advantages of polymeric precursors, the bulk BC structure can be tailored to NWs by choosing the correct precursor ratio and suitable synthesis temperature. In this research work, a low-temperature condensation method is selected to synthesize BC NWs using readily available natural carbon source, castor oil.

2 Experimental

Of different synthesis methods for the formation of NWs, the solution-based approach is more suitable. The structure can be controlled by varying the precursor ratio and synthesis temperature. The use of organic precursors, for the formation of BC, facilitates the dispersibility and uniformity of boron and carbon sources. Among boron sources, boric acid enhances the esterification process due to the liberation of hydroxyl groups [31, 36]. For the synthesis of BC, boric acid (Sigma-Aldrich) and castor oil (Indian pharmaceuticals) are used as the boron and carbon sources in the ratio of 1:4, respectively, by condensation reaction method. Initially, boric acid is added to the heated castor oil. The mixture is refluxed with the help of a heating mantle at a temperature of 75–80 °C until all the moisture content is vaporized from the mixture. The mixture's golden yellow gel is transferred to white solid after the reaction and is subjected to pre-treatment at 300 °C for three hours to get the dry powder. The crushed powder is then heat-treated at 900 °C for two hours in a tubular furnace with a continuous nitrogen gas flow. The obtained powder is annealed at 600 °C in the air (1 h) to remove unreacted carbon to get the BC sample.

The BC sample synthesized is subjected to different morphological, structural, and compositional analyses using field emission scanning electron microscope (FESEM - Nova Nano), X-ray diffractometer (XRD - Bruker d8 Advance), and Fourier transform infrared spectrometer (FTIR - Thermo Fisher iS50) in attenuated total reflectance mode in the region 4000 – 400 cm^{-1} . The product's optical properties are also studied by UV-visible absorption (UV-Vis- Jasco V550) and photoluminescence (PL- Horiba Fluoromax) spectroscopic methods.

3 Results And Discussion

The formation of 1D BC NWs can be understood from the FESEM images shown in Fig. 1. The morphological modifications of the sample before and after the heat treatment at 900 °C are analyzed.

From Fig. 1, the transformation of morphology to 1D NWs, upon annealing to 900 °C, is evident. The images given at different magnification (nm to μm scale) indicate the formation of NWs over a large area. Figure 1 also reveals the formation of 1D NWs, of diameter 14 nm and length up to 750 nm, at 900 °C from the nanolayers appearing at 300 °C. A closer examination of the NWs (from Fig. 1(d)) reveals a beaded chain morphology responsible for the surface roughness.

(c) and (d) annealed at 900 °C.

The structure of the compounds formed is identified through the XRD analysis. The XRD pattern of the sample with NW morphology (Fig. 2) shows a high-intensity peak at 27.5° due to the orthorhombic BC (ICDD file No. 00-026-0232) and the peaks at 30° , 34° , 39° , 42° , 54° , 60° , 66° indicated the presence of rhombohedral BC (ICDD file No. 00-019-0178 and 00-035-0798). When compared to standard patterns, the broadening and shifting of peaks at 34° and 39° can be attributed to the crystal defect, twins [37–40]. The FTIR spectrum, Fig. 3, showing the molecular species' vibrational modes can be used for understanding the structure of the sample. The characteristic peak at 1398 cm^{-1} present in the BC NWs is assigned to boron icosahedra, indicating more boron in the sample. When the peaks around 627 and 1190 cm^{-1} correspond to the B-C stretching vibration, those in the region $550 - 410\text{ cm}^{-1}$ (shown as an inset of Fig. 4) show the C-B-C bending vibrations [35, 41]. B-C and C-B-C bands' presence indicates the complete reaction between boric acid and castor oil with the formation of borate ester bonds and hence confirms the formation of boron rich BC. The other bands around 3200 cm^{-1} and

2260 cm^{-1} are assigned to $-\text{OH}$ and C-O stretching vibrations.

The determination of the bandgap energy of BC is essential for its application in electronics and optoelectronics. The variation in the stoichiometry of BC varies the bandgap from 0.4 eV to 2.7 eV [41–43]. Figure 4(a) shows the UV-Vis absorption spectrum of the BC NW and shows a maximum absorption around 265 nm due to the $\text{C}=\text{O}$ $n-\pi^*$ transition in the sp^3 hybrid region. The direct bandgap energy of the BC NWs calculated from the Tauc plot (Fig. 4(b)) is obtained as 2.08 eV. The PL spectrum of BC NWs, Fig. 5(a), for the excitations at 270 nm and 300 nm shows a broad emission with the peak centered around 410 nm. The human eye's color perception can be understood from the CIE plot [44] shown in Fig. 5(b). The CIE coordinates for the two excitations (0.148,0.039) and (0.144,0.047) fall in the chromaticity diagram's blue region. The distribution of emitted energy at different wavelengths can be understood from the power spectrum shown in Fig. 5(c) and (d).

(c) the power spectrum for λ_{ex} - 270 nm and (d) power spectrum for λ_{ex} - 300 nm.

4 Conclusion

The present paper reports the low-temperature green synthesis of BC NWs by condensation method using castor oil as the carbon precursor. The 1D BC nanostructures have emerged as an important class of technologically significant material. Of various synthesis methods, employing sophisticated equipment

and toxic chemicals, eco-friendly approaches are highly relevant and became the focus of research. As an organic precursor, castor oil facilitates the dispersibility with boric acid, boron source, and forms the NWs through the condensation reaction. The FESEM analysis of the BC NWs exhibit beaded chain morphology of diameter 14 nm and length 750 nm. The UV-Vis spectroscopic analysis indicates a direct bandgap of energy 2.08 eV. The XRD analysis shows a high-intensity peak at 27.5° due to the orthorhombic BC, and the peaks at 30°, 34°, 39°, 42°, 54°, 60°, 66° suggests the presence of rhombohedral BC. The FTIR spectrum shows the B-C stretching vibration and C-B-C bending vibrations confirming the nanowire to be boron carbide. The PL spectrum recorded for the excitations 270 and 300 nm shows a peak at 410 nm. The CIE plot shows the coordinates corresponding to the emission (0.148,0.039) and (0.144,0.047) in the blue region. The attractive thermal, physical, and electrical properties of BC NWs make it suitable in power applications and as cathode materials. Thus, the study reveals the possibility of green synthesis of 1D BC NWs using castor oil as the natural carbon source for potential photonic and electronic applications.

Declarations

Acknowledgment

The author H.V. Saritha Devi is grateful to Kerala State Council for Science, Technology and Environment (KSCSTE) for the financial support.

References

1. Meyyappan M, Sunkara MK (2009) Inorganic Nanowires: Applications, Properties, and Characterization. CRC Press, Boca Raton
2. Guisbiers G, Mejía-Rosales S, Leonard Deepak F (2012) Nanomaterial Properties: Size and Shape Dependencies. *J Nanomater*. <http://doi.org/10.1155/2012/180976>
3. Dasgupta NP, Sun J, Liu C et al (2014) 25th Anniversary Article: Semiconductor Nanowires—Synthesis, Characterization, and Applications. *Adv mater* 26:2137–2184
4. McIlroy DN, Alkhateeb A, Zhang D et al (2004) Nanospring formation—unexpected catalyst mediated growth. *J Phys Condens Matter* 16:415–440
5. Zhang Y, Ram MK, Stefanakos EK et al (2012) Synthesis, Characterization, and Applications of ZnO Nanowires. *J Nanomater*. <http://dx.doi.org/10.1155/2012/624520>
6. Zhang X, Wang G, Liu X et al (2008) Different CuO nanostructures: synthesis, characterization, and applications for glucose sensors. *J Phys Chem C* 112:16845–16849
7. Xia Y, Yang P, Sun Y et al (2003) One-Dimensional Nanostructures: Synthesis, Characterization, and Applications. *Adv Mater* 15:353–389
8. Devan RS, Patil RA, Lin JH et al (2012) One-dimensional metal-oxide nanostructures: Recent developments in Synthesis, Characterization, and Applications. *Adv Funct Mater* 22:3326–3370

9. Khalil A, Singh Lalia B, Hashaichek R et al (2013) Electrospun metallic nanowires: Synthesis, characterization, and applications. *J Appl Phys* 114:171301
10. Cheng C, Fan HJ (2012) Branched nanowires: synthesis and energy applications. *Nano Today* 7:327–343
11. Mondal S, Banthia AK (2005) Low-temperature synthetic route for boron carbide. *J Eur Ceram Soc* 25:287–291
12. Suri AK, Subramanian C, Sonber JK et al (2010) Synthesis and consolidation of boron carbide: a review. *Int Mater Rev* 55:4–40
13. Sariyer D, Küçer R, Küçer N (2015) Neutron shielding properties of concretes containing boron carbide and ferro–boron. *Procedia-Social Behavioral Sciences* 195:1752–1756
14. Liu LL, He GG, Wang YH et al (2017) Ignition and Combustion Performance of the Primary Condensed-phase Combustion Products from Boron-based Fuel-rich Propellants. *Cent Eur J Energ Mater* 14:1–13
15. Saritha Devi HV, Swapna MS, Raj V et al (2018) Natural cotton as precursor for the refractory boron carbide—a hydrothermal synthesis and characterization. *Mater Res Express* 5:015603
16. Saritha Devi HV, Swapna MS, Ambadas G et al (2018) Hydrothermal development and characterization of the wear-resistant boron carbide from *Pandanus*: a natural carbon precursor. *Appl Phys A* 124:297
17. Saritha Devi HV, Swapna MS, Ambadas G et al (2018) Low-temperature green synthesis of boron carbide using aloe vera. *Chin Phys B* 27:107702
18. Tao X, Dong L, Wang X et al (2010) B₄C-Nanowires/Carbon-Microfiber Hybrid Structures and Composites from Cotton T-shirts. *Adv Mater* 22:2055–2059
19. Ji-Fa T, Li-Hong B, Xing-Jun W et al (2008) Probing field emission from boron carbide nanowires. *Chin Phys Lett* 25:3463
20. Huang Y, Liu F, Luo Q et al (2012) Fabrication of patterned boron carbide nanowires and their electrical, field emission, and flexibility properties. *Nano Res* 5:896–902
21. Zhang Y, Zhang Y, Gong H et al (2016) Microwave-assisted sol–gel synthesis of neutron-absorbed nano-sized ¹⁰B-enriched B₄C powders. *J Sol-Gel Sci Technol* 80:683–689
22. Sneddon LG, Pender MJ, Forsthoefel KM et al (2005) Design, syntheses and applications of chemical precursors to advanced ceramic materials in nanostructured forms. *J Eur Ceram Soc* 25:91–97
23. Li-Hong B, Chen L, Yuan T et al (2008) Synthesis and photoluminescence property of boron carbide nanowires. *Chinese Phys B* 17:4585–4507
24. Rodríguez MG, Kharissova OV, Ortiz-Mendez U (2004) Formation of boron carbide nanofibers and nanobelts from heated by microwave. *Rev Adv Mater Sci* 7:55–60
25. Chang B, Gersten BL, Szewczyk ST et al (2006) Towards the preparation of boron carbide nanorods by carbothermal reaction method. In *NSTI-Nanotech* 1:369–372

26. Velamakanni A, Ganesh KJ, Zhu Y et al (2009) Catalyst-Free Synthesis and Characterization of Metastable Boron Carbide Nanowires. *Adv Funct Mater* 19:3926–3933
27. Ma R, Bando Y (2002) Investigation on the growth of boron carbide nanowires. *Chem Mater* 14:4403–4407
28. Pender MJ, Forsthoefel KM, Sneddon LG (2003) Molecular and polymeric precursors to boron carbide nanofibers, nanocylinders, and nanoporous ceramics. *Pure Appl Chem* 75:1287–1294
29. Zhang D, McIlroy DN, Geng Y et al (1999) Growth and characterization of boron carbide nanowires. *J Mater Sci Lett* 18:349–351
30. Ma R, Bando Y (2002) High purity single crystalline boron carbide nanowires. *Chem Phys Lett* 364:314–317
31. Rafi-ud-din, Zahid GH, Asghar Z et al (2014) Ethylene glycol assisted low-temperature synthesis of boron carbide powder from borate citrate precursors. *J Asian Ceram Soc* 2:268–274
32. Amir F, Naser E, Mehdi R et al (2012) Synthesis of boron carbide nano particles using polyvinyl alcohol and boric acid. *Ceram – Silik* 56:32–35
33. Shawgi N, Wang S, Wang Z et al (2017) Synthesis of nano particles and fiber-like shape boron carbide powder from ploy (vinyl alcohol) and boric acid. *J Sol-Gel Sci Technol* 82:450–457
34. Saritha Devi HV, Swapna MS, Sankararaman S (2020) Cost-Effective Green Synthesis of Boron-Rich Carbide Coatings for Infrared Windows and Night-Vision Optics. *Phys Status Solidi A* 217:1901014
35. Wang S, Li Y, Xing X et al (2018) Low-temperature synthesis of high-purity boron carbide via an aromatic polymer precursor. *J Mater Res* 33:1659–1670
36. Saritha Devi HV, Swapna MS, Ambadas G et al (2018) Low temperature synthesis of multilayered-hollow microspheres of boron carbide from castor oil for photonic applications. *J Appl Phy* 124:065303
37. Anselmi-Tamburini U, Munir ZA, Kodera Y et al (2005) Influence of synthesis temperature on the defect structure of boron carbide: experimental and modeling studies. *J Am Ceram Soc* 88:1382–1387
38. Fujita T, Guan P, Madhav Reddy K et al (2014) Asymmetric twins in rhombohedral boron carbide. *Appl Phys Lett* 104:021907
39. Jazirehpour M, Alizadeh A (2009) Synthesis of Boron Carbide Core – Shell Nanorods and a Qualitative Model To Explain Formation of Rough Shell Nanorods. *J Phys Chem C* 113:1657–1661
40. Guan Z, Gutu T, Yang J et al (2012) Boron carbide nanowires: low temperature synthesis and structural and thermal conductivity characterization. *J Mater Chem* 22:9853–9860
41. Domnich V, Reynaud S, Haber RA et al (2011) Boron carbide: structure, properties, and stability under stress. *J Am Ceram Soc* 94:3605–3628
42. Werheit H, Binnenbruck H, Hausen A (1971) Optical Properties of Boron Carbide and Comparison with b-Rhombohedral Boron. *Phys Status Solidi B* 47:153–158

43. Bylander DM, Kleinman L, Lee S (1990) Self-consistent calculations of the energy bands and bonding properties of $B_{12}C_3$. *Phy Rev B* 42:1394
44. Saritha Devi HV, Swapna MS, Ambadas G et al (2018) Optical Emission Diagnosis of Boron Carbide Synthesized Using Natural Carbon Precursors. *Opt Spectrosc* 125:928

Figures

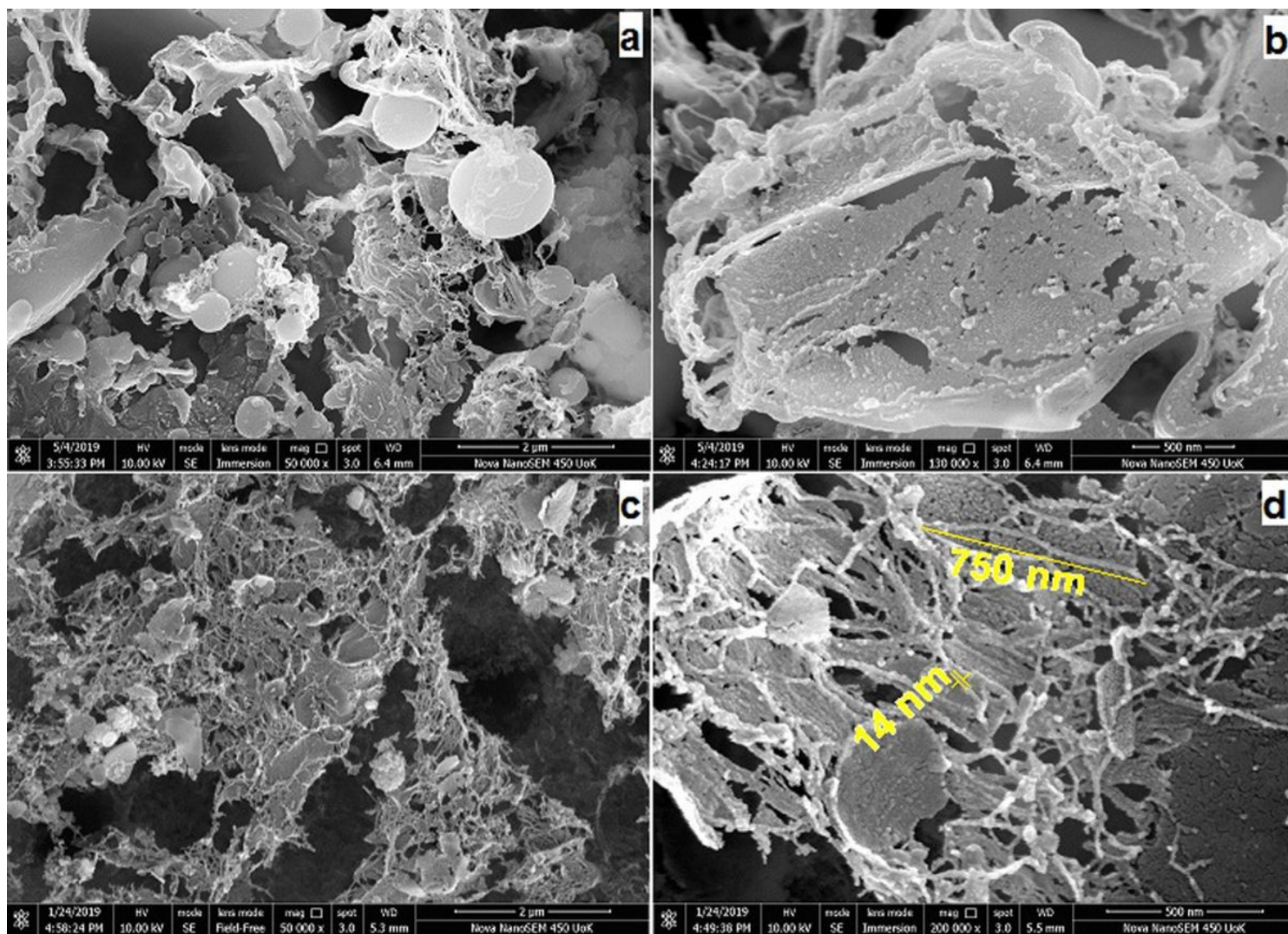


Figure 1

FESEM images of the sample: (a) and (b) annealed at 300 °C; (c) and (d) annealed at 900 °C.

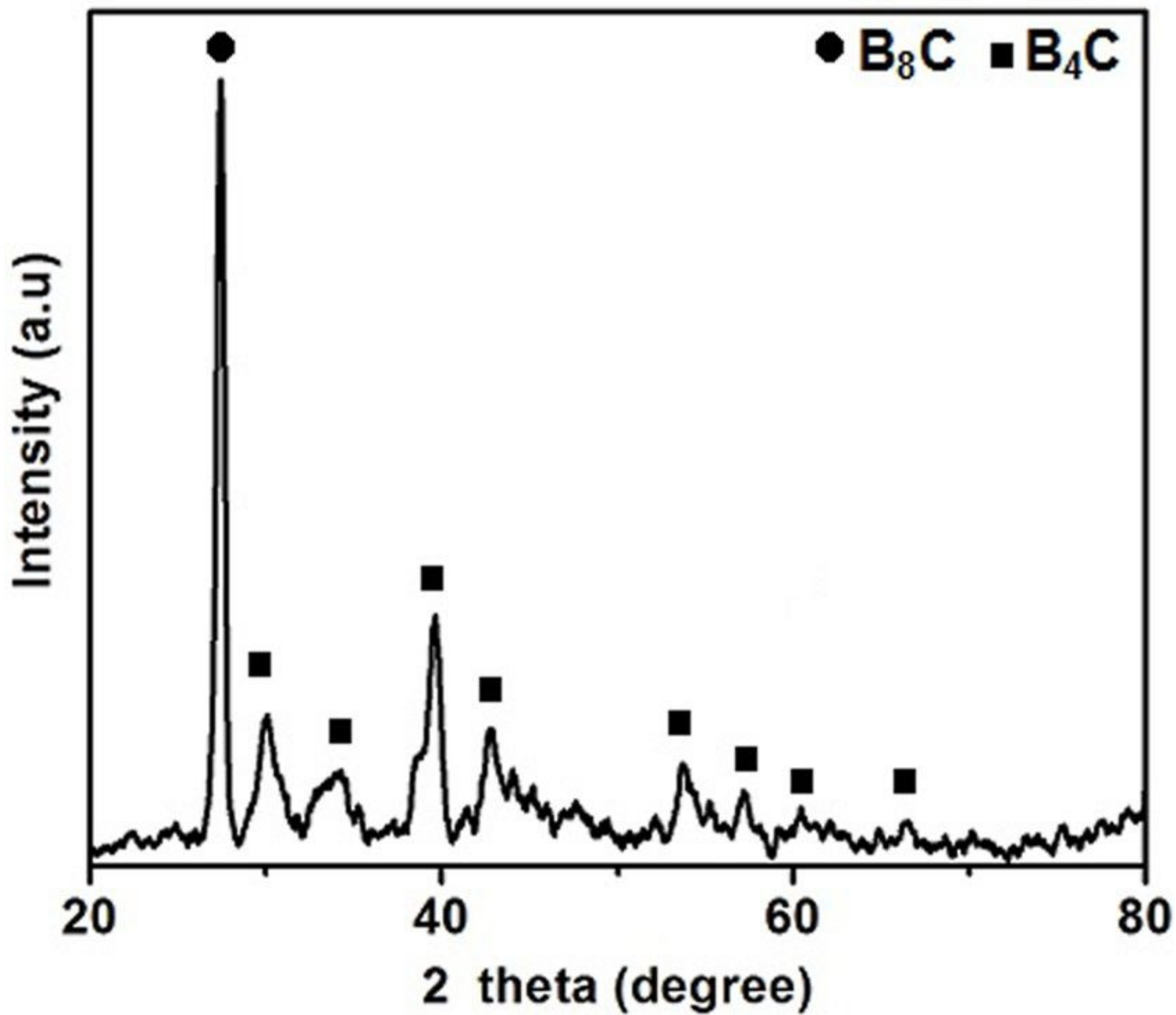


Figure 2

XRD pattern of the BC nanowires synthesized

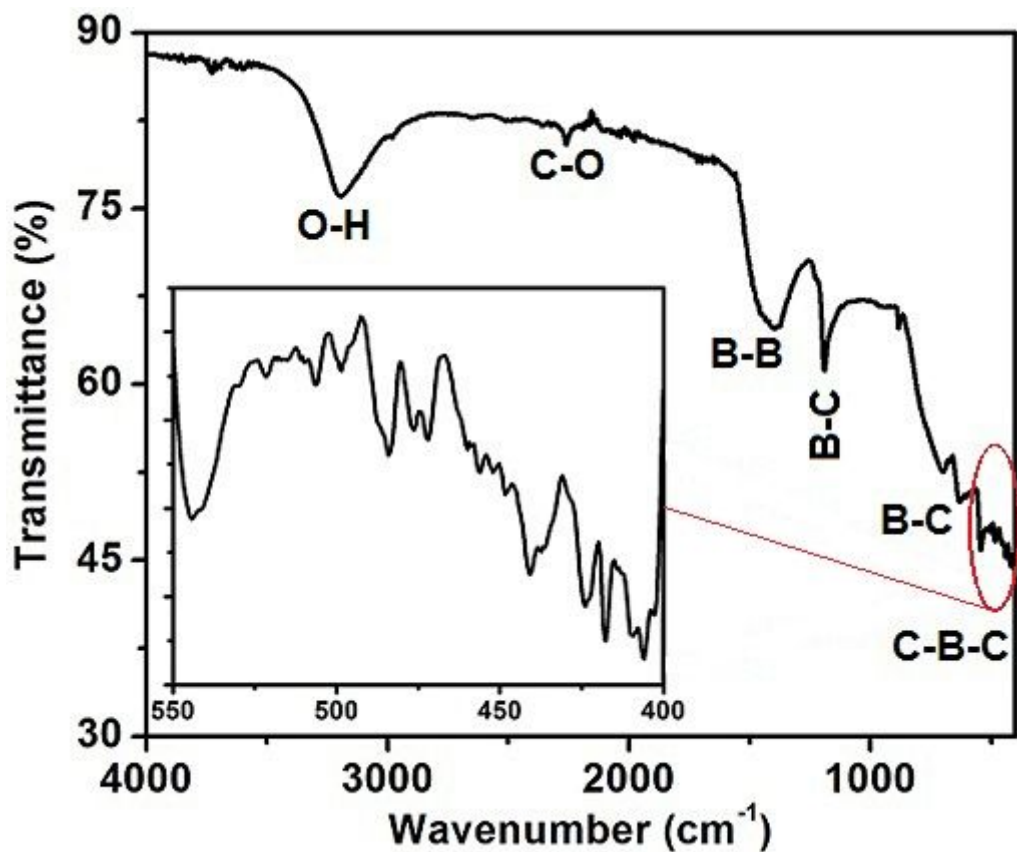


Figure 3

FTIR spectrum of the BC nanowires synthesized.

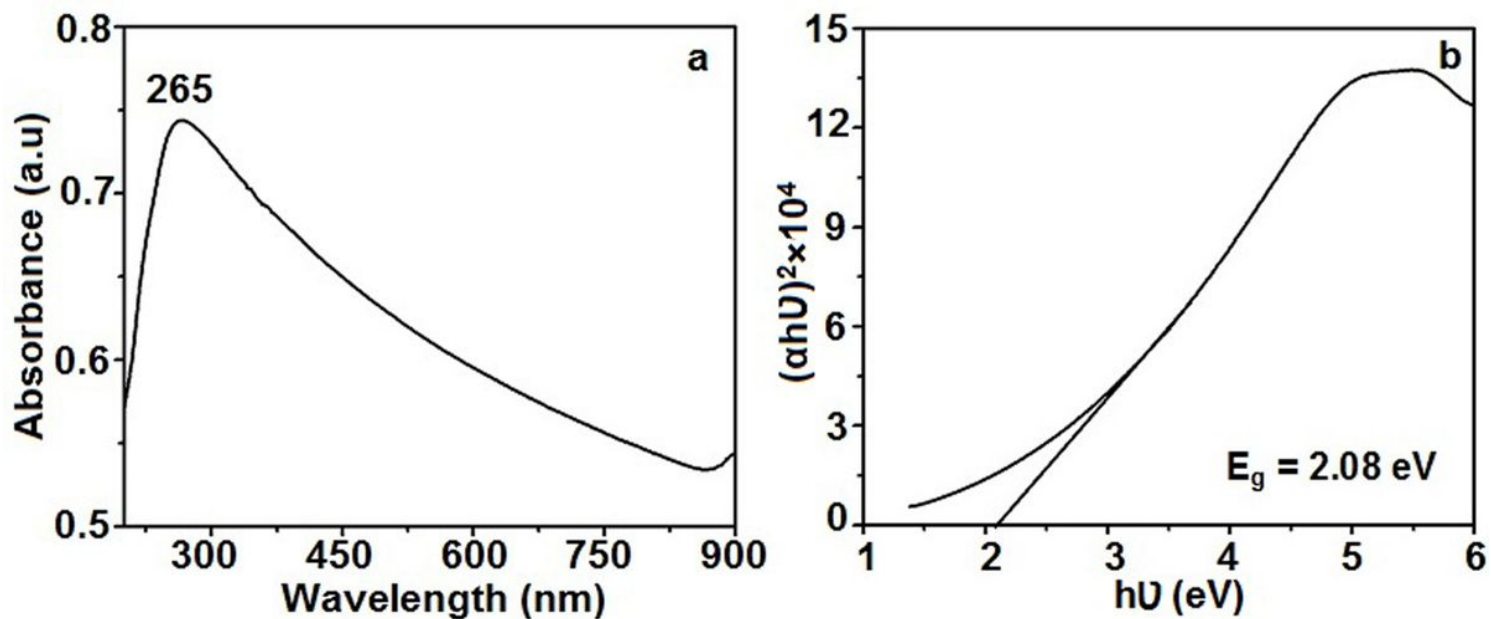


Figure 4

BC NWs - (a) UV-Vis absorption spectrum and (b) Tauc plot.

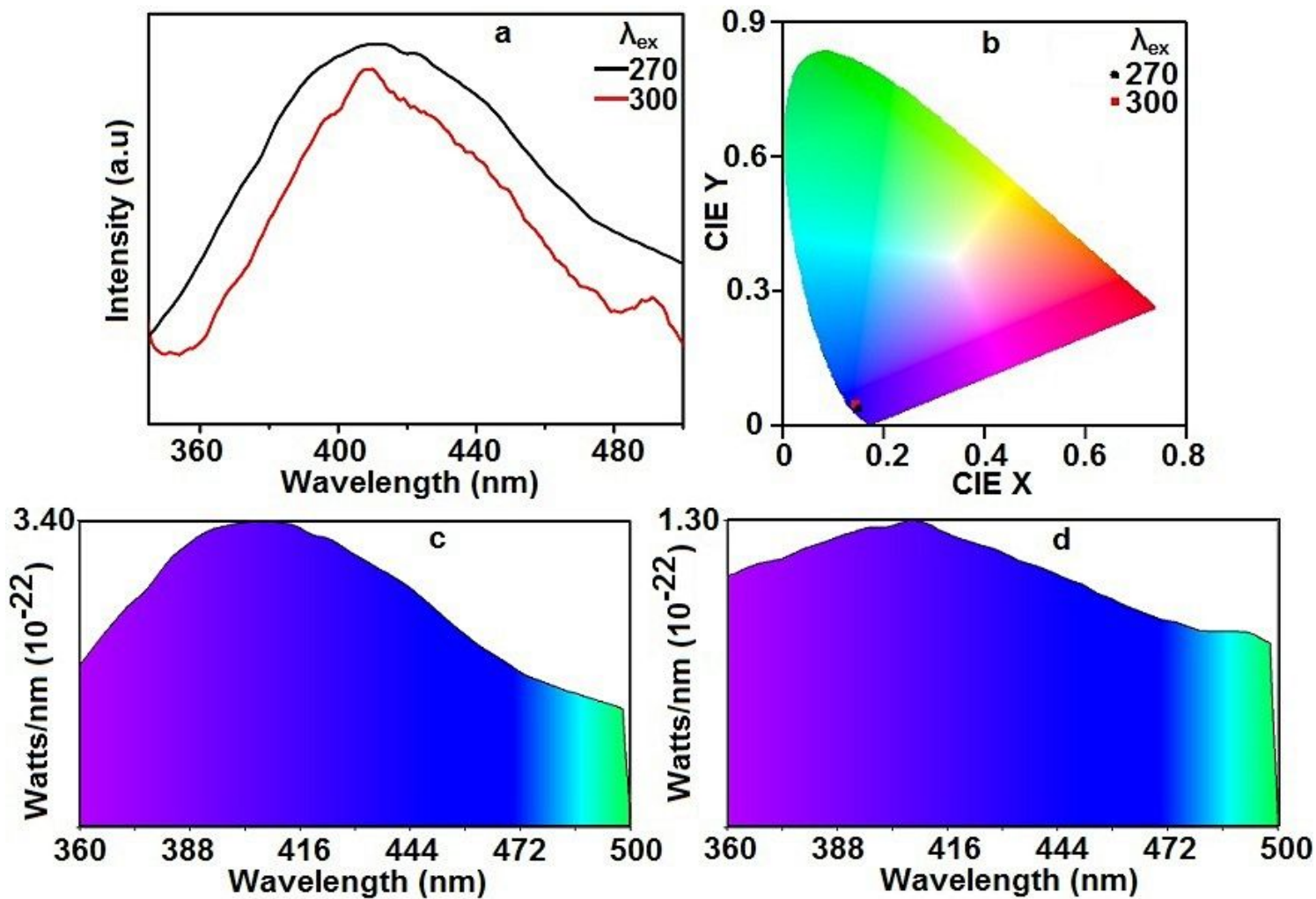


Figure 5

(a) PL spectra of BC NWs for λ_{ex} - 270 nm and 300 nm, (b) CIE plot, (c) the power spectrum for λ_{ex} - 270 nm and (d) power spectrum for λ_{ex} - 300 nm.