

Microwave Synthesis of Boron Nitride Nanostructures

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Abstract — One dimensional boron nitride nanostructures promise many interesting applications in biomedical, semiconductor and hydrogen storage and other fields. We have synthesized Boron Nitride in various nanoforms by a high temperature solid state reaction between boric acid and urea in a commercial microwave furnace. The formation of boron nitride was established from the binding energies for boron and nitrogen obtained from its X-Ray Photoelectron spectrum. The structural phase of the product was confirmed by X-Ray diffraction and Fourier Transform Infrared spectroscopy. Transmission Electron Microscopy revealed that BN nanowires of about 20 nm diameter with very high aspect ratios of the order of 100:1 and also nanotubes were obtained.

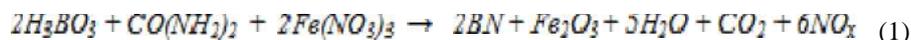
Keywords- boron nitride; nanotube; nanowire; microwave synthesis; branched nanotube

I. INTRODUCTION

Nanostructures such as nanowires and nanotubes have generated significant interest particularly after the great application potentials of the carbon nanotubes (CNTs) were recognized. Subsequently, Boron nitride, in its hexagonal phase being structurally analogous to graphite, received attention regarding its nanostructural forms similar to CNTs. Many studies have been reported on the synthesis of boron nitride nanostructures with different morphologies such as nanotubes^[1], nanocages^[2], nanorods and nanowires^[3], porous structures^[4], and hollow spheres^[5]. In fact, Boron Nitride nanotube (BNNT) with very good thermal and chemical stability^[6] enjoys a superiority over CNTs in certain applications. Among many synthetic techniques adopted for nanostructures, the microwave assisted solid state synthesis^{[7][8]} is a rapidly developing novel method. This paper discusses the synthesis of Boron Nitride nanowires (BNNWs) and nanotubes by microwave heating of solid precursors and the details of various characterizations carried out on the resultant.

II. EXPERIMENTAL

In this work BN was prepared using a mixture of boric acid (H_3BO_3) and urea ($CO(NH_2)_2$) in 1:5 molar ratio in the presence of a small quantity (~ 0.1 mole) of iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), as a catalyst. The above mixture was taken in an alumina crucible and kept inside a ceramic susceptor which was subjected to microwave heating at a rate of $10^\circ C/min$ in an ambient atmosphere till attaining about $1000^\circ C$. The mixture was maintained at this temperature for 20 min in order to ensure completion of reaction. Reaction with oxygen in this ambience was unavoidable. Any resultant contaminants were sought to be removed by thoroughly washing with de-ionized water and diluted hydrochloric acid. The end product was collected by filtration and dried at room temperature. The following reaction reported^[9] earlier for a similar synthesis procedure is expected to have driven the formation of boron nitride in our experiment also.



III. RESULTS AND DISCUSSION

A. X-ray Diffraction (XRD)

All XRD analyses were carried out on a Rich Seifert diffractometer Model TT3000 using $CuK_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ \AA}$). The as synthesized product was first analyzed and the pattern (not shown here) obtained revealed the presence of impurities which corresponded to boron oxide and iron oxide. After proper cleaning as described above the XRD pattern was again obtained (Fig.1). This pattern indicated the complete removal of boron oxide whereas iron oxide (marked with *) [PDF # 72-0469]^[10] could not be totally removed. However, h- BN phase formation could be established from the peak present at $2\theta \sim 26.6^\circ$ in this pattern (marked with #), though weak [PDF # 85-1068]^[10].

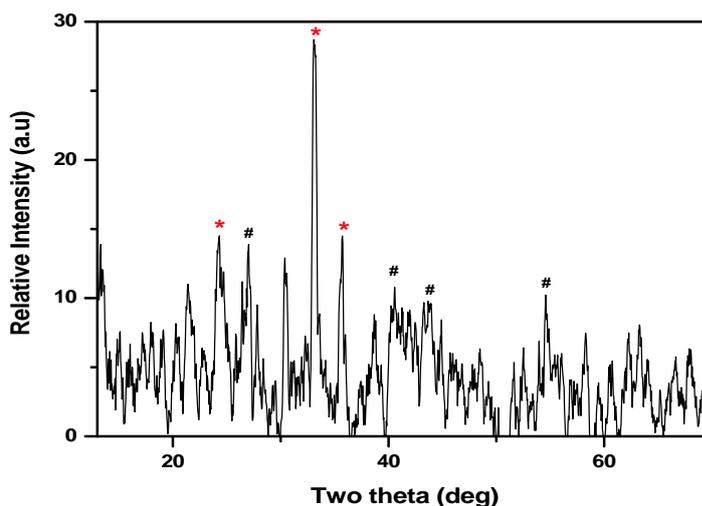


Figure 1. X-ray diffraction pattern obtained for the end product after thorough washing. The h-BN peaks are marked by # whereas * indicates peaks from the remnant Fe₂O₃.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectral scans were all obtained at room temperature using the Spectrum RX 1 model spectrometer from PERKIN ELMER, USA. The absorption peaks corresponding to B-O stretch, B-O strain and O-B-O bending appearing in The FTIR spectrum (not shown here) of the as prepared sample corroborated the presence of oxide impurities inferred earlier from XRD. The FTIR spectrum (Fig.2) of the reaction product, after thorough washing as described above was free of these impurity peaks. Fig. 2 further exhibited absorption peaks at 785 cm⁻¹ and 1400 cm⁻¹. These could be attributed to B-N-B bending and B-N stretching in hexagonal boron nitride^{[11][12][13]}. The sharp absorption peaks located at 2345 cm⁻¹ and 2367 cm⁻¹ could be assigned to C≡N; and the broad peak centered at 3428 cm⁻¹ to N-H or O-H group^[14]. Thus both XRD and FTIR characterizations helped in identifying the impurity phases and also in confirming the h-BN formation.

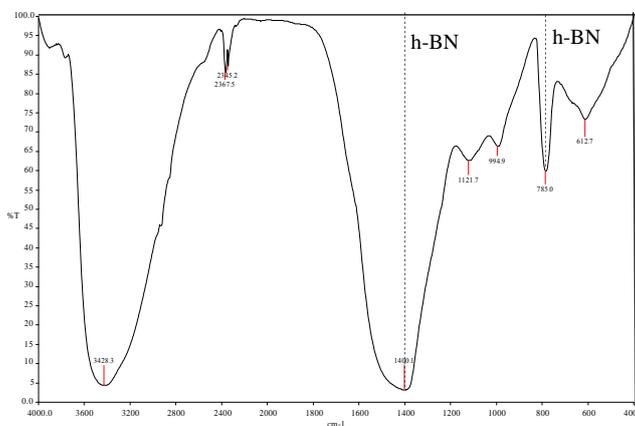


Figure 2 The FTIR spectrum obtained for boron nitride synthesized by microwave assisted solid state reaction after thorough washing; the absorption peaks corresponding to h-BN are labeled.

B. X-Ray Photoelectron spectroscopy (XPS)

XPS analysis was carried out for the washed BN sample on an Omicron ESCA probe spectrometer, using Al K monochromatic (Energy=1486.6 eV) source. The survey scan (not shown) contained peaks from boron, nitrogen and adventitious carbon as well as silicon and considerable oxygen primarily from the glass sample holder. The high resolution spectra for B1s and N1s regions are shown in Fig.3 (a) and 3(b) respectively. The double humped B1s spectrum was deconvoluted to obtain its component peaks at 190.1 and 192.8 eV. The peaks located at 190.1 eV (Fig.3a) and 397.3 eV (Fig. 3b) and ascribed to B 1s and N1s respectively, correspond to binding energies responsible for B-N bond formation^{[15][16]}. The deconvoluted B 1s peak at 192.8 eV falls within the range of binding energy values experimentally observed for B-O bonding^[17].

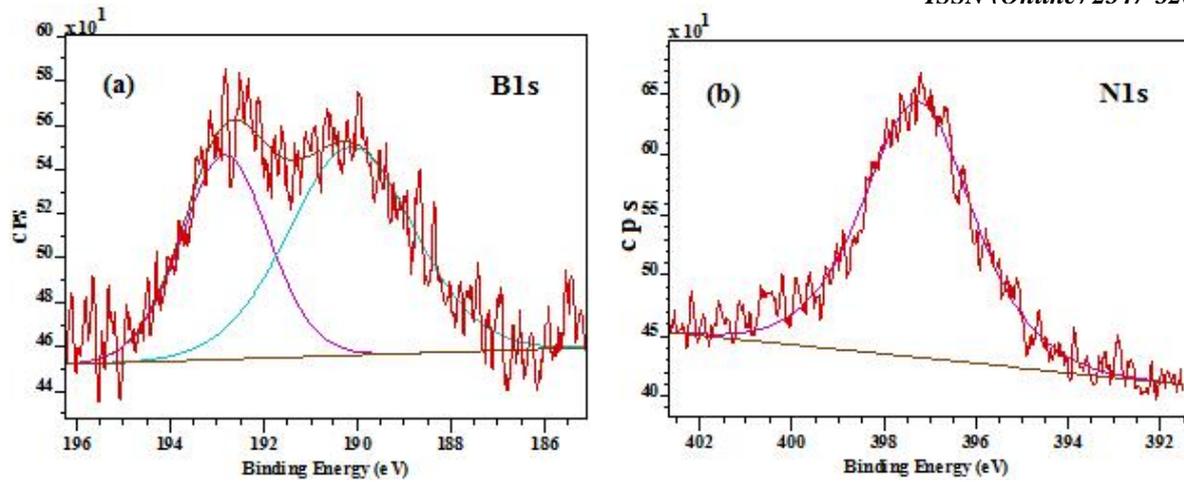


Figure. 3 High resolution XPS spectra for B1s and N 1s region for microwave assisted boron nitride nanorods and nanowires.

Transmission Electron Microscopy

High resolution transmission electron micrographs (HRTEM) of boron nitride at three different magnifications are shown in Fig. 4. The low magnification image (Fig. 4a) shows long wire-like morphologies of various lengths ranging from 1-4 μm . The high magnification image (Fig. 4c) reveals h-BN nanowires (BNNWs), nanotubes (BNNTs) and also bamboo like morphologies all uniformly of diameter $\sim 18\text{ nm}$. The high aspect ratio of NWs (1:100) indicates that MW synthesis can yield h-BN nanostructures of high integrity. The zoomed pictures of the locations marked A and B in Fig 4c are exhibited in Fig 4d. The region A in Fig.4d suggests that the cross sections of BNNTs are almost circular and the tips of the tubes are densely filled with Fe_2O_3 , catalyst for BNNTs growth. The region B pictures an unusual nanotube structure with a branched junction somewhere half-way along its length. A highly magnified view (Fig. 4b) of the nanowire shows that the surface of nanowire is rough, decorated with Fe_2O_3 particles. Lattice fringes obtained on these dark particles confirmed that they are Fe_2O_3 particles.

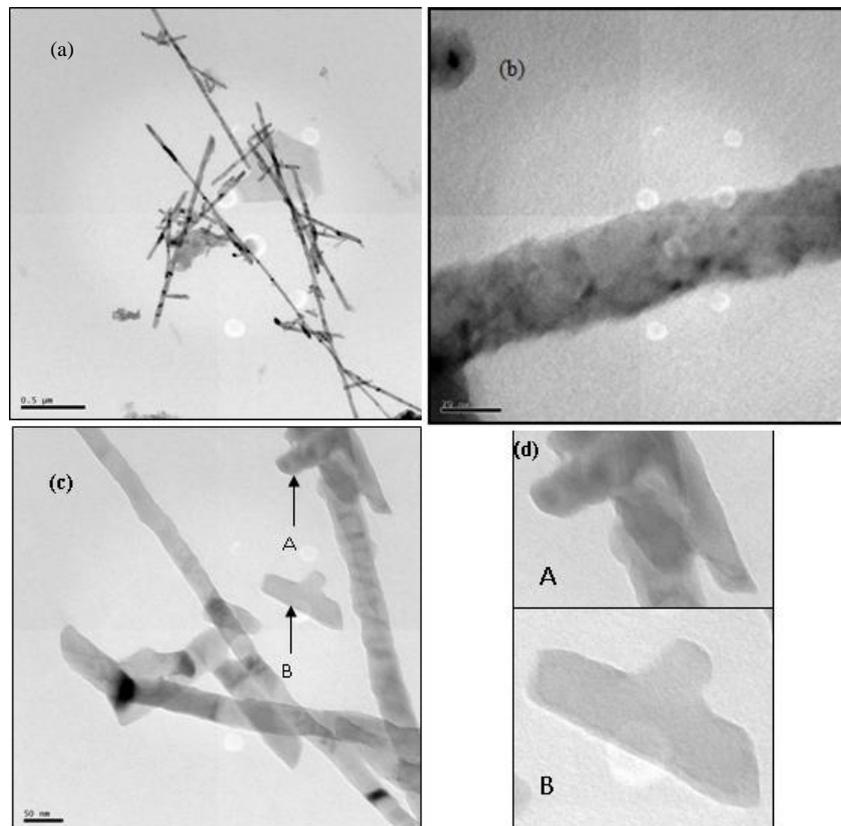


Figure 4. HRTEM images of Boron nitride synthesized microwave assisted solid state reaction showing (a) 18 nm dia nanowires of high aspect ratio, (b) wire decorated with catalyst iron oxide nanoparticles and (c) and (d) nanotube seen with iron oxide capping in a bent (A) form and a T-branched nanotube (B)

IV. CONCLUSION

Boron nitride nanowires and nanotubes were obtained by reacting boric acid and urea at 1000 °C in an ambient atmosphere using commercial microwave furnace. XRD and FTIR characterizations helped in identifying the impurity phases and further in confirming the h-BN formation. From HRTEM it is seen that nanowires and nanotubes of uniform diameter are produced. The nanotubes are strong enough to be stable in a bent formation and are capped with iron oxide particles, the nucleation catalysts. The unusual T-shaped nanotube with a branching in the middle is a new tube morphology not yet reported for BNNT to be best of our knowledge.

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