Solvothermal synthesis of carbon nanotube-B_2O_3 nanocomposite using tributyl borate as boron oxide source

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Abstract

Single-walled carbon nanotube-B_2O_3 nanocomposite has been prepared using solvothermal technique. Tributyl borate was explored as the boron oxide reagent using toluene and water as the solvent, respectively. Characterization of the reaction products using Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction and thermogravimetric analysis confirmed the formation of the CNT-B_2O_3 nanocomposite. The solvothermal approach may serve as a facile strategy for synthesis of nanocomposites of metal oxides and carbon nanotubes especially when metal alkoxides is utilized as precursor for the metal oxides.
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Keywords: Nanocomposite; Solvothermal; Tributyl borate; Boric oxide; Carbon nanotube

Carbon nanotubes have outstanding mechanical, electrical, thermal, optical/spectroscopic properties and chemical reactivity [1–9]. Exploitation of these numerous potentials for practical purposes has not been fully realized, largely because of the need to control the surface chemistry in other to effectively modulate specific properties, most especially in nanocomposites. To effectively utilized CNTs in inorganic matrix, we have to significantly modify the surface for matrix compatibility and ease of dispersion.

Various strategy have been reported in modulating surface of CNTs to improve matrix dispersion, such techniques includes covalent functionalization [10,11], coating of various inorganic compounds, for example, nanoparticle oxides of $Al(OH)_3$, Al_2O_3, SnO_2, SiO_2, and TiO_2 in order to expand the scope of their potential applications [12–16]. Boric oxide is an important refractory material, and when in the glassy crystalline state shows resistance to solvents and chemicals, additionally it is a useful cladding material over the core material with a lower refractive index as wave guides in the transmission of electromagnetic waves in optical communication systems [17]. Therefore, deposition of boron oxide on carbon nanotubes surface can produce a new range of materials with potential application in nanoelectronics technology [18–22]. Previously, the synthesis of CNTs-B_2O_3 nanocomposite required the autoclaving of commercially available B_2O_3 with CNTs [23]. In this communication, we report a facile approach to coat CNTs with boric oxide powder starting from (less expensive) boric acid to obtain CNTs-B_2O_3 nanocomposite. Carbon nanotubes used in this work was obtained from Carbon nanotubes Inc. (CNI, USA), from lot # XD 3365 A, which contains, about 33% single-walled CNTs and some double and multi walled carbon nanotubes and less than 55 metal oxide impurities. The synthesis of $(n\text{-}C_4H_9O)_3B$ precursor was accomplished using the modified literature procedure as reported [24]. The CNTs-B_2O_3 nanocomposite was prepared using solvothermal process, with toluene serving as the solvent [24].

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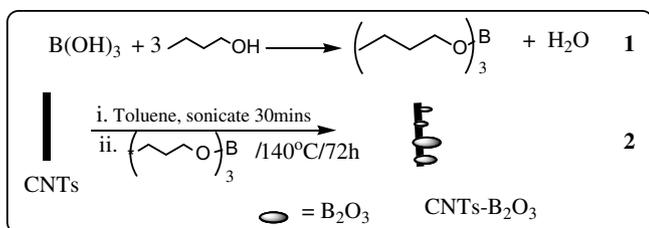
Fig. 1. Reaction schemes for tributyl borate mediated SWCNT-B_2O_3 nanocomposite.
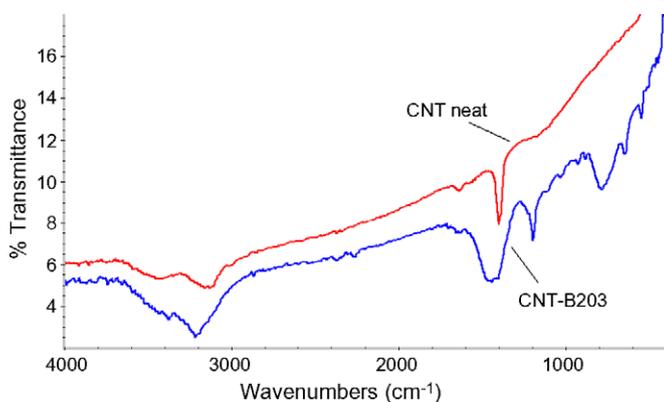
Fig. 2. FTIR of CNTs coated with B_2O_3 compared with neat CNTs.

The synthesis of CNTs-B_2O_3 nanocomposite based on the facile solvothermal protocol is summarized in Fig. 1.

The FTIR spectra of the nanocomposite materials are shown in Fig. 2. The spectrum for CNTs-B_2O_3 shows B_2O_3 characteristic peaks at 1458, 1195, and 795 cm^{-1}, respectively [25]. X-ray powder diffraction data identify the B_2O_3 crystalline phase present in the sample under

45 kV and 40 mA with copper kα radiation. The analysis indicates that the most intense peak corresponds to the boron oxide in Fig. 3.

The TEM picture of the CNTs-B_2O_2 is shown in Fig. 4, and clearly shows that the coatings of CNT with boron oxide also help detangled and un-roped the carbon nanotubes. The thermogravimetric analysis (TGA) performed on approximately 10 mg samples is shown in Fig. 5. The run consisted of a ramp at a steady rate of 25 °C/min from 40 °C to 800 °C in nitrogen. The analysis shows two sharp weight losses at about 100 °C and 620 °C, respectively. The first weight loss of about 27% is likely due to solvents, while the second weight loss is probably due to oxidation of exposed carbon on the CNTs defect sites. The TGA analysis of pristine CNTs (not shown) shows one sharp weight loss that drops to about 2% at 600 °C. We can infer from the residual weight loss for the nanocomposite that the surface B_2O_3 prevents complete decomposition of the carbon nanotubes [23]. The reaction of tributyl borate with CNTs under similar condition but utilizing water as the solvent (hydrothermal) was also explored as a strategy to the desired CNTs-B_2O_3 nanocomposite. However, this approach resulted in the hydrolysis of tributyl borate to boric acid, and the deposition of boric acid on CNTs.

In summary, we have reported a simple technique to coat CNTs with B_2O_3 with potential applications in nanocomposite technology. This method can also be utilized to improve the dispersion of CNTs in inorganic matrix and may generally be extended to other metal oxides. We are currently investigating the potential applications of this materials in nanoelectronic industry. It is envisioned that this solvothermal approach may serve as a facile strategy for synthesis of nanocomposites of metal oxides and carbon nanotubes using metal alkoxides as starting reagents.
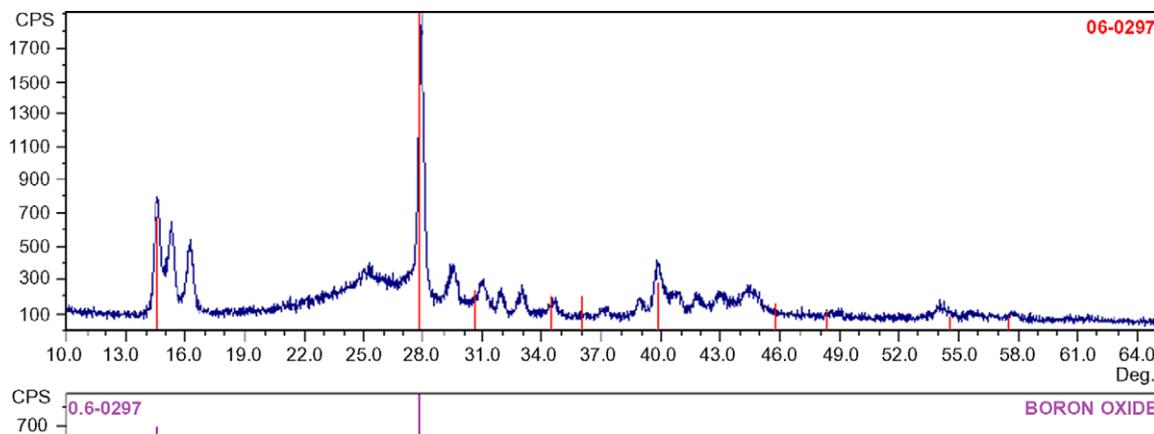
Fig. 3. X-ray powder diffraction analysis of CNTs-B_2O_3 confirms boron oxide.
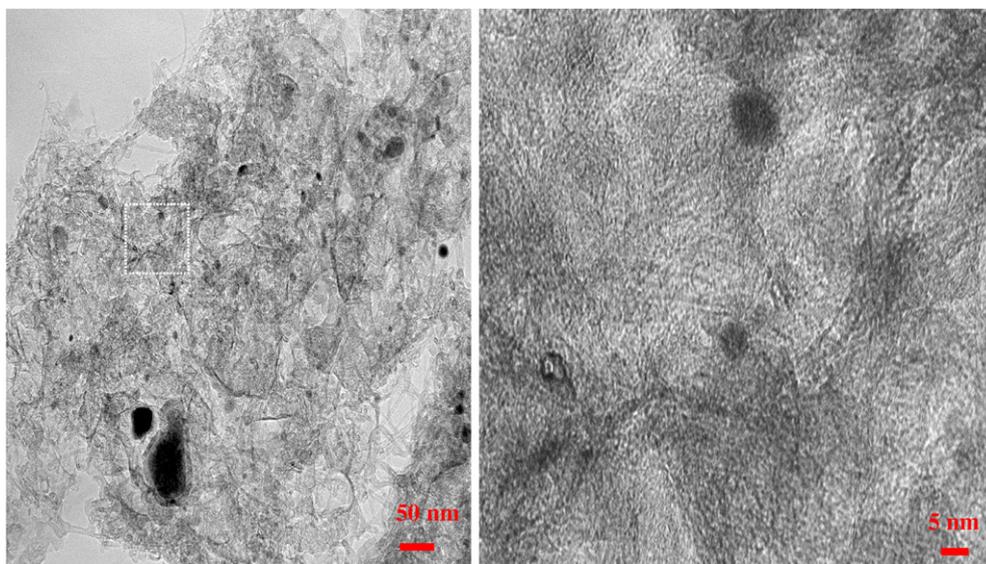
Fig. 4. TEM of CNTs-B$_2$O$_3$ nanocomposite.
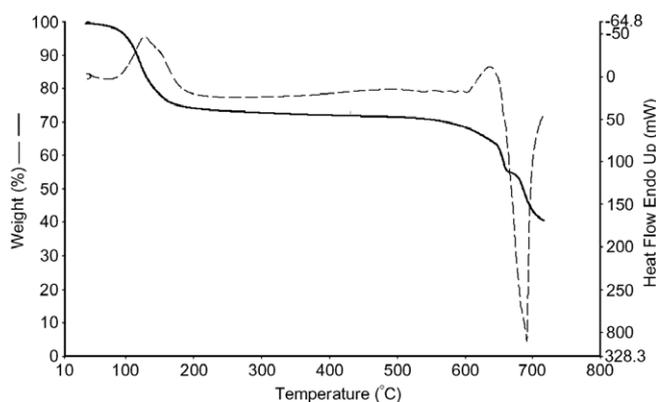
Fig. 5. TGA for CNTs-B$_2$O$_3$ nanocomposite.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007. 12.015.

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[24] To a one necked 250 ml round bottom flask equipped with a Dean–Stark receiver and reflux condenser was added 18.0 g (294.87 mmol) of H$_3$BO$_3$, 87.43 g (1179.51 mmol) of n-C$_4$H$_9$OH and 50 ml of toluene. The resulting mixture was heated at 130 °C for 5 h. The Dean–Stark receiver was detached and the product mixture was distilled at 226–228 °C under 1 atm pressure to collect 59.0 g (257.23 mmol, 80% yield) H.I. Schlesinger, H.C. Brown, D.L. Mayfield, J.R. Gilbreath, J. Am. Chem. Soc. 75 (1953) 213. For the synthesis of CNTs-B$_2$O$_3$ nanocomposite, To a 40 ml Teflon coated steel reactor was added CNTs about 30.0 mg and 15 ml of toluene. The suspension was sonicated for 30 min to disperse the CNTs. Thereafter, 0.5 g of (n-C$_4$H$_9$O)$_3$B (2.18 mmol) was added before heating at 140 °C for 96 h. The reaction was cooled to room

temperature and the suspension filtered through a 0.2 μm membrane under vacuum. The black residue obtained was washed with toluene, and dried at 100 °C for 24 h. The product was characterized by FTIR in KBr (model IR-200 Thermo-Nicolet 2.2), XRD (model Scintag theta–theta diffractometer PAD-X), and TGA (model Universal V3.4C TA instruments).

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