Effect of boron concentration on physicochemical properties of boron-doped carbon nanotubes

Godfrey Keru, Patrick G. Ndungu, Vincent O. Nyamori*

School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban, 4000, South Africa

HIGHLIGHTS

- Boron-doping of carbon nanotubes (CNTs) changes their physiochemical properties.
- Amount of boron-doping was dependent on the wt.% of boron precursor used.
- Boron-doping changed CNTs surfaces and the distribution of dispersive energy sites.
- Boron-doping affected the conductivity and ferromagnetic properties.
- Increased boron-doping results in a more favourable interaction with polar probes.

ARTICLE INFO

ABSTRACT

Boron-doped carbon nanotubes (B-CNTs) were synthesized using chemical vapour deposition (CVD) floating catalyst method. Toluene was used as the carbon source, triphenylborane as boron as well as the carbon source while ferrocene was used as the catalyst. The amount of triphenylborane used was varied in a solution of toluene and ferrocene. Ferrocene was kept constant at 2.5 wt.%. while a maximum temperature of 900 °C was used for the synthesis of the shaped carbon nanomaterial (SCNMs). SCNMs obtained were characterized by the use of transmission electron microscope (TEM), scanning electron microscope (SEM), high resolution-electron microscope, electron dispersive X-ay spectroscopy (EDX), Raman spectroscopy, inductively coupled plasma-optical emission spectroscopy (ICP-OES), vibrating sample magnetometer (VSM), nitrogen adsorption at 77 K, and inverse gas chromatography. TEM and SEM analysis confirmed SCNMs obtained were a mixture of B-CNTs and carbon nanofibres (B-CNF). EDX and ICP-OES results showed that boron was successively incorporated into the carbon hexagonal network of CNTs and its concentration was dependent on the amount of triphenylborane used. From the VSM results, the boron doping within the CNTs introduced ferromagnetic properties, and as the percentage of boron increased the magnetic coactivity and squareness changed. In addition, boron doping changed the conductivity and the surface energy among other physicochemical properties of B-CNTs.

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1. Introduction

Doping carbon nanotubes is a process of introducing foreign atoms into the carbon backbone structure to deliberately fine tune their physicochemical properties. Doping of carbon nanotubes (CNTs) with heteroatoms such as boron or nitrogen alters their chemical [1], electrical [2], mechanical [3] and physical properties [4]. In addition, it also increases the number of defects on the walls of the CNTs; breaking inertness and enhancing reactivity [5].

Mousavi and Moradian [6] reported increased electrical conductivity of CNTs with increased nitrogen- or boron-dopant concentration. The increase in boron-doping has been found to enhance crystallinity [7] and improve field emission properties when compared to pristine and nitrogen-doped CNTs [8]. Enhanced properties after doping CNTs with boron has resulted in the application of these materials in; hydrogen storage [9], oxygen reduction reactions [10], transparent conducting film [2], secondary batteries [11] and field emitters [12] among others.

Boron-doping of CNTs can be achieved through either; post—or direct-synthesis. In post-synthesis doping, already synthesized CNTs are mixed with the boron-dopant, normally at high temperature, inducing substitution of carbon with the boron [13].

However, this has a disadvantage of introducing undesirable by-products such as nano-rods that form during this high temperature process [14]. On the other hand, direct-synthesis boron-doping can be achieved by heating a mixture of boron-dopant, carbon source and the catalyst. Examples of boron sources in direct-synthesis doping include boron trioxide [15], boron fluoride [16], organoboranes [7,17–19] or diborane [20]. This process can be achieved by the arc discharge [21,22], laser ablation [13,23] and chemical vapour deposition (CVD) [16,24] methods. Organoboranes are more popular with the CVD method because they do not only supply boron but can also be an additional source of carbon. CVD is the most preferred synthesis method because it is economical, possible to scale up and easier to fine tune doping levels by simply controlling various physical parameters such as temperature and pressure while also the chemical aspect such as concentration of the dopant in the precursors mixture [7].

It is also possible, with the CVD method, to synthesize preferred dimensions and the level or concentration of boron within the boron-doped CNTs (B-CNTs). For example Lyu et al. [7] synthesized double-walled CNTs with boron concentration ranging between 0.8 and 3.1 atomic % (at.%) by catalytic decomposition of tetrahydro-furan, triisopropylborane over Fe–Mo/MgO catalyst. Alternatively, B-CNTs were synthesized by CVD using benzene, triphenylborane and ferrocene as catalyst with boron content ranging between 0 and 2.24% [10].

In this paper we report for the first time effect of boron concentration in the B-CNTs on the surface energy properties of these materials. To the best of our knowledge the influence of boron-doping on the surface energy of B-CNTs has not been reported. Inverse gas chromatography (IGC) is a very versatile and reliable technique for determination of surface characteristics of a material since they can be compared and quantified. From these results energetic properties of sample surfaces and functional groups attached can be determined. CNTs can be used as fillers with other compounds such as polymers, or as components in other types of nanocomposites. Surface energy properties can be linked to various physical–chemical properties that can provide some insights into which compounds (gases, liquids, or solids) can interact with CNTs to ensure their unique properties can be well utilised.

2. Experimental

2.1. Materials and synthesis of B-CNTs

All the chemicals used in this study were of analytical grade and were used as received unless stated otherwise. Both triphenylborane (98%) and ferrocene (98%) were purchased from Sigma Aldrich Co. (St Louis, USA) and toluene (97%) from BDH chemicals (Poole England). For all samples ferrocene catalyst weight percent (wt.%) was constant i.e. at 2.5 wt.% while, triphenylborane concentration was varied 1.0, 2.5 and 5.0 wt.%. Toluene as a carbon source was added to make 100 wt.%. The total mass of the mixture was 10 g and was placed in a 20 mL plastic syringe. Reactor set-up used was based on a previously reported design [25]. In brief, a quartz tube (inner diameter 27 mm and length 850 mm) was used as the reactor vessel. This was placed inside a tube furnace (model no. TSH12/50/610, Elite Thermal Systems Ltd.) fitted with a main zone furnace controller (Eurotherm 2416). The furnace was heated to a maximum temperature (T_{max}) of 900 °C, and a mixture of toluene, triphenylborane and ferrocene was injected at a flow rate of 0.8 mL min^{-1} using a syringe pump (New Era Inc. syringe pump, model no. NE 300). The carrier gas used was a mixture of 10% hydrogen in argon (v/v) and was set at a flow rate of 100 mL/min. The product was obtained from the part of quartz tube reactor that was in the hot zone of tube furnace, weighed, before being

characterised. Iron catalyst nanoparticles and amorphous carbons were purified from as-synthesized products by refluxing with 6 M HNO$_3$. 200 mg of as-synthesized products was mixed with 50 mL 6 M HNO$_3$ in a round bottomed flask. The mixture was stirred at 80 °C for 12 h, vacuum filtered, washed with distilled water several times until the pH of the filtrate was 7 then dried in a vacuum at 100 °C for 12 h.

2.2. Characterizations

The carbon products obtained were characterised using several instruments. Initial analysis on the surface morphology was conducted using a field emission scanning microscope (Carl Zeiss Ultra Plus). Samples were pressed onto double sided carbon tape mounted on aluminium stubs, placed within the microscope and then analysed using an accelerating voltage of 10 kV. Images were captured using the Zeiss ultra plus FEGSEM software. Further structural and morphological characterizations were done using a JEOL transmission electron microscope (JEOL, TEM 1010) and a high-resolution transmission electron microscope (HR-TEM) (JEOL, JEM 2100) using accelerating voltages of 100 and 200 kV respectively. Before TEM or HR-TEM analysis, samples were dispersed in ethanol using a bath sonicator and then were drop dried on carbon coated copper grids. On the TEM, images were captured using Megaview 3 camera and then analysed using iTEM software. On the HR-TEM, Gatan digital micrograph software was used for imaging while electron dispersive X-ray spectroscopy (EDX) which was coupled to the instrument (INCA 4.15 by Oxford instrument) was used for qualitative elemental analysis.

Raman spectroscopy on the carbon products was done using a DeltaNu Advantage 532™ Raman spectrometer. The excitation source was a Nd: YAG solid state crystal class 3b diode laser at 532 nm excitation wavelength. Nuspec ™ software was used to capture generated spectra. Thermogravimetric analysis (TGA) was done using TA Instrument Q series ™ Thermal analyser DSC/TGA (Q600). The carbon products obtained were heated at a rate of 10 °C min^{-1} using an air flow rate of 50 mL min^{-1}, and the data was captured and analysed using the TA instrument universal analysis 2000 software.

The boron content and its percentage or concentration in the carbon products were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a Perkin Elmer Optima 5300 DV. 10 mg of B-CNTs samples were digested in piranha solution (a mixture of conc sulphuric acid and 30% v/v hydrogen peroxide in the ratio 3:1). The WinLab 32 software was used to analyse the data.

Magnetic properties were determined using vibrating sample magnetometer (VSM) and the data was analysed by the VSM system software. Conductivity was calculated from resistivity obtained by four probe resistivity measurements (Scientific equipment and service, India). Samples were prepared by dispersing 30 mg of carbon products in 10 mL of ethanol using bath sonication for 30 min. The dispersion was vacuum filtered with a hitch funnel to form a thin film of about 0.15 mm (±0.01) on the filter paper. The film thickness was determined using micrometre screw gauge. In brief, the samples were fixed on the four probes then inserted in proportional-integral-derivative (PID) controlled oven. The controller minimizes the temperature error by adjusting upward or downward in case of over shoot. Temperature was varied between room temperature and 110 °C at 3° interval each time recording change in voltage while current was kept constant.

Textural characteristics were determined using Micrometrics TriStar II surface area and porosity while the data was captured and analysed using TriStar II 3020 Version 2 Software. Samples were weighed (200 mg) and vacuum degassed for 12 h before