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Production and Study of Boron and Nitrogen-doped Carbon Nanotubes by Arc Discharge Method Using Dispersive Raman Back-Scattering Spectroscopy

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Raman scattering studies reveal the remarkable structure and the unusual electronic and phonon properties of carbon nanotubes (CNTs). In this study, we directly produced boron and nitrogen doped CNTs by using DC-arc discharge method which normally can be employed for producing CNTs. An experiment was performed without the catalyst and in the presence of Ar gas for producing boron doped CNTs. At the second and third stages and in the presence of Al_2O_3 and MgO as catalysts and nitrogen, N_2 gas were used for producing nitrogen doped CNTs. In general, present investigation revealed that some major changes caused by boron and nitrogen dopants can be observed in the related recorded Raman spectra.

Key Words: Raman spectroscopy, Boron and Nirtogen doped carbon nanotubes, DC-Arc discharge method.

INTRODUCTION

Element carbon present in the sp^2 hybridization can form a variety of amazing structures. Apart from the well-known graphite, carbon can build closed and open cages with honeycomb atomic arrangement. First such structure was discovered as the fullerene molecule C_{60} by Kroto *et al.*[1]. Although various carbon cages were studied, it was only in 1991, when Sumio Iijima[2] observed for the first time tubular carbon structures. The nanotubes considered of up to several tens of graphitic shells (so-called multi-walled carbon nanotubes (MWNTs))with adjacent shell separation of *ca.* 0.34 nm, diameters of *ca.* 1 nm and large length/diameter ratio. Iijima and Ichihashi[3] and Bethune *et al.*[4] synthesized single-walled carbon nanotubes (SWNTs) (Fig. 1). Nowadays MWNTs and SWNTs are produced mainly by three techniques: arc-discharge, laser-ablation and catalytic growth. The synthesized nanotube samples are characterized by means of Raman, electronic and optical spectroscopies. Important information is derived by mechanical, electrical and thermal measurements. The experimental data is discussed in comparison with the results of theoretical models[5-7].

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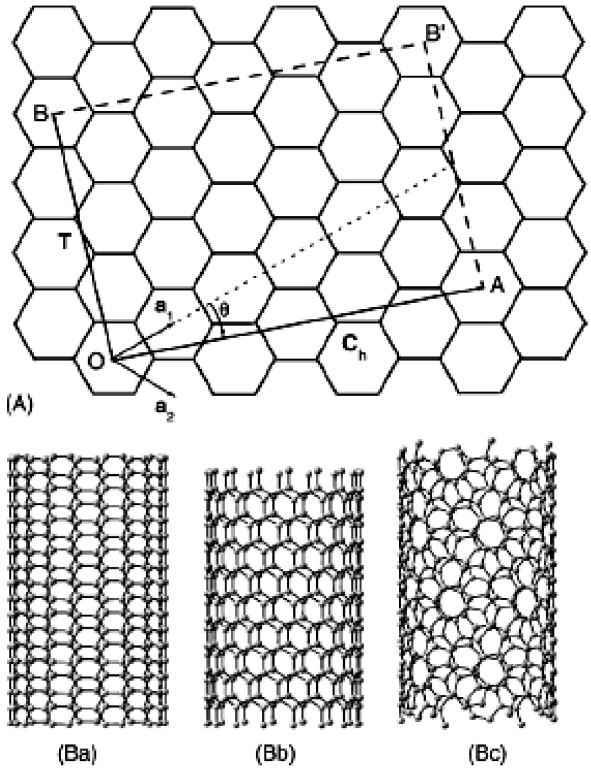

Fig. 1. Schematic representation of construction by rolling-up an infinite strip of graphite sheet (so-called grapheme)

The construction of a nanotube by rolling-up an infinite strip of graphite sheet (so-called graphene) is shown in Fig. 1.

In (A) the chiral vector $C_h = na_1 + ma_2$ connects two lattice points O and A on the graphene sheet (n and m are integer numbers and a_1 and a_2 are basic vectors of unit cell of graphene). An infinite strip is cut from the sheet through these two points, perpendicular to the chiral vector. The strip is then rolled-up into a seamless cylinder. $T = t_1a_1 + t_2a_2$ is the primitive translation vector of the tube[8], where t_1 and t_2 are coefficients related to (n, m). The nanotube is uniquely specified by the pair of integer numbers n, m or by $R = C_h/2\pi$ and chiral angle θ which is the angle between C_h and the nearest zigzag of C-C bonds. All different tubes have angles θ between zero and 30º. Special tube types are the achiral tubes (tubes with mirror symmetry): armchair tubes (n, n) (θ = 30º) (B(a)) and zigzag tubes (n, 0) (θ = 0º) [B(b)]. All other tubes are called chiral [B(c)]. Details about relations between structural parameters of CNTs can be found in work of Dresselhaus *et al.*[9].

Raman spectroscopy is a powerful tool for characterizing the unique optical properties of carbon nanotubes. Raman scattering reveals structural and unusual electronic, phonon properties and metallic and semiconductor phases of carbon

nanotubes[10-12]. This investigation has proven to be a very useful probe of carbon-based materials and has been used extensively to study the bonding and semi-conducting and super conducting phases of CNTs and also changes caused by different doping levels. In this work, we have produced the B and N doped CNTs samples by arc discharge method (Fig. 1) and investigated the samples by this method by using the dispersive Raman back-scattering spectroscopy.

Characteristics of Raman Spectra of CNTs: Basically the most characteristics Raman spectra bands of CNTs are as follows (Fig. 2)[13-15]: (1) A band at low frequencies which is called Radial Breathing Mode (RBM) and correspond to the coherent vibration of the C atoms in the radial direction[16,17], as if the tube was 'breathing' and whose frequency ω_{RBM} is about 100-500 cm^{-1}. This frequency is proportional to the nano tubes diameters and is expressed[18,19] as $\omega_{RBM} = 248/d_t$ cm^{-1}. (2) A band at higher frequency so-called disordered-induced D mode that is observed[20,21] at *ca.* 1350 cm^{-1}. (3) A peak, so-called G mode and is observed at about 1600 cm^{-1}, usually divided to two peaks or bands at higher frequencies related to the atomic vibrations along the circumferential direction and along their axis direction, respectively, which are called G^+mode and G^-mode and are seen both in semiconductor and metallic tubes[10-13,22]. (4) A peak or a band observed as the first overtone of D-mode which is mostly defined by G'mode and is observed[23,24] at *ca.* 2450 cm^{-1}.

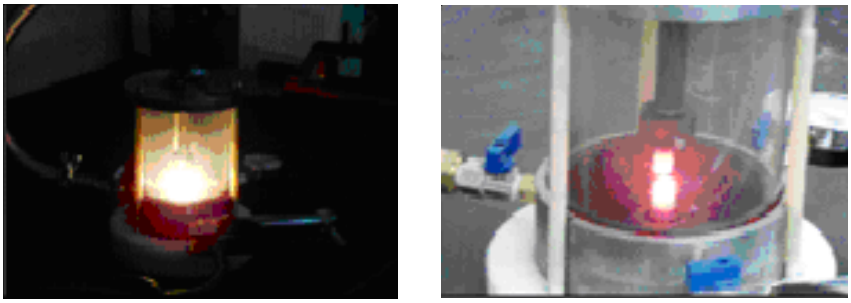

Fig. 2. Schematic representation of apparatus used to produce CNTs samples

In present study, we directly produced boron, B and nitrogen, N, doped CNTs by using DC-arc discharge method which normally can be employed for producing CNTs. First, we performed a experiments without the catalyst and in the presence of Ar gas for producing boron doped CNTs. At the second and third stages and in the presence of Al_2O_3 and MgO as catalysts and N_2 gas were used for producing nitrogen doped CNTs.

Doping effects: Boron and nitrogen are the nearest elements to carbon in the periodic table, doping of graphite with such elements will modify the electronically, mechanical and oxidative properties of these materials and offer the opportunity not only to understand dopants induced perturbation in physical properties of one dimensional materials but such doping also provides an opportunity to exploit their

unique properties in the next generation of doping technologies with boron and nitrogen which are respectively expected to behave as a acceptor (p-type) or donor (n-type) dopants and enhance CNTs conductivity[10,11].

EXPERIMENTAL

The doped carbon nanotubes sample used in this study were prepared by DC arc discharge method. Primarily, anode electrode was a graphite rod with 4.5 mm diameter and 3 cm length which was drilled for constructing a hole with 2.25 mm diameter and depth with a ratio of 2/3 of electrode length. Cathode electrode also was a graphite rod with 2.5 mm diameter and 3 cm in length.

In the first stage of present experiments and for producing boron doped carbon nanotubes we used an argon atmosphere and graphite powder as the carbon source and without using catalyst particles, we filled the hole of the anode with a suspension of ethanol solution and boron and graphite powders at the C/B ratio of 2/3 by weight. The DC currents of 110, 120 and 130 ampere in a gas flow of 20 sccm of Ar were employed. The dark grey filamentous material deposited on the cathode electrode were collected and were purified by rinsing in acid and heating in a furnace at a suitable temperature.

In the second stage we produced nitrogen doped carbon nanotubes at N_2 atmosphere by using Al_2O_3 as catalyst powder at Al_2O_3/C ratio of 3/97 by weight (3 % Al_2O_3 and 97 % graphite) in weight. The DC currents of 100, 120 and145 ampere in a gas flow of 1000 milll/min of N_2 were employed. Similar first stage the samples in this stage were collected and were purified.

In the next stage and for producing nitrogen doped carbon nanotubes MgO as catalyst in nitrogen atmosphere was used. The related molecular weight of MgO and C was 3 % MgO and 97 % C in ethanol alcohol suspension in with DC currents 110, 120 and 130 ampere in a gas flow of 1000 mL/min of N_2 were employed. The samples after collection were purified with acid and heating. The samples produced of every stage after purification were examined by Raman spectroscopy (Figs. 3-5).

RESULTS AND DISCUSSION

In Fig. 4, Raman spectra of boron doped CNTs in the absence catalyst in argon atmosphere has been presented. The measure of G-mode frequency and D-modes frequency due to this spectrum are 1611 and 1374 cm^{-1}, respectively that have increased in comparison with G-mode and D-mode frequencies of spectrum of non doped CNTs that are 1600 and 1350 cm^{-1} respectively[10,22].

The reasons of increase of G-mode and D-mode frequencies are these, (1) because the boron atoms capture additional electrons from neighbouring carbon atoms (as an acceptor) cause strengthen the bond of B-C and so the G-mode frequency transfer to higher frequencies, (2) and also the increase of D-mode frequency causes increase disorder in structure of CNTs.

In Fig. 4 existence of several RBM-modes show that this CNTs is MWNTs whereas in Fig. 5 existence of two RBM-modes show that this CNTs is DWNTs.

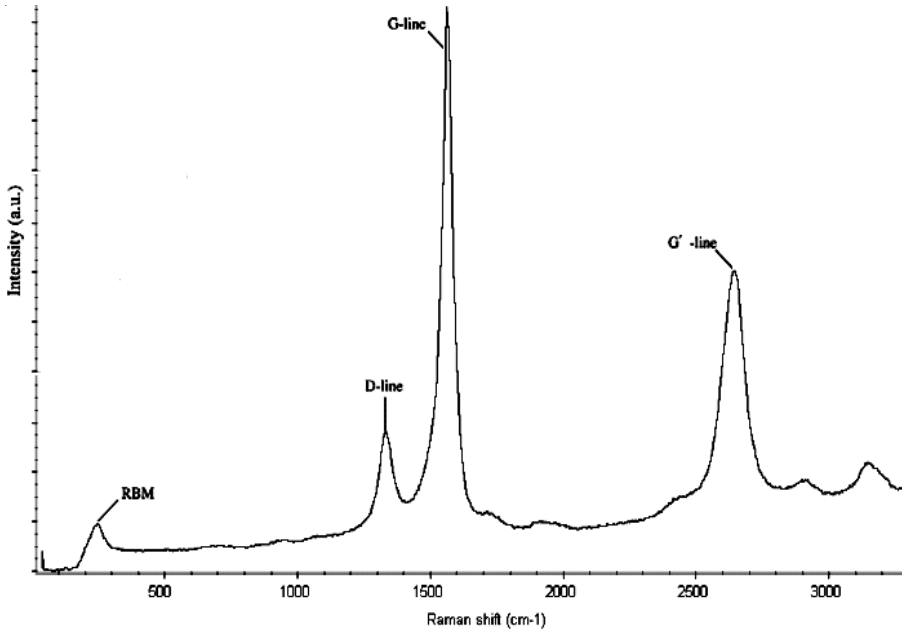

Fig. 3. Characteristic Raman peaks of non doped CNTs

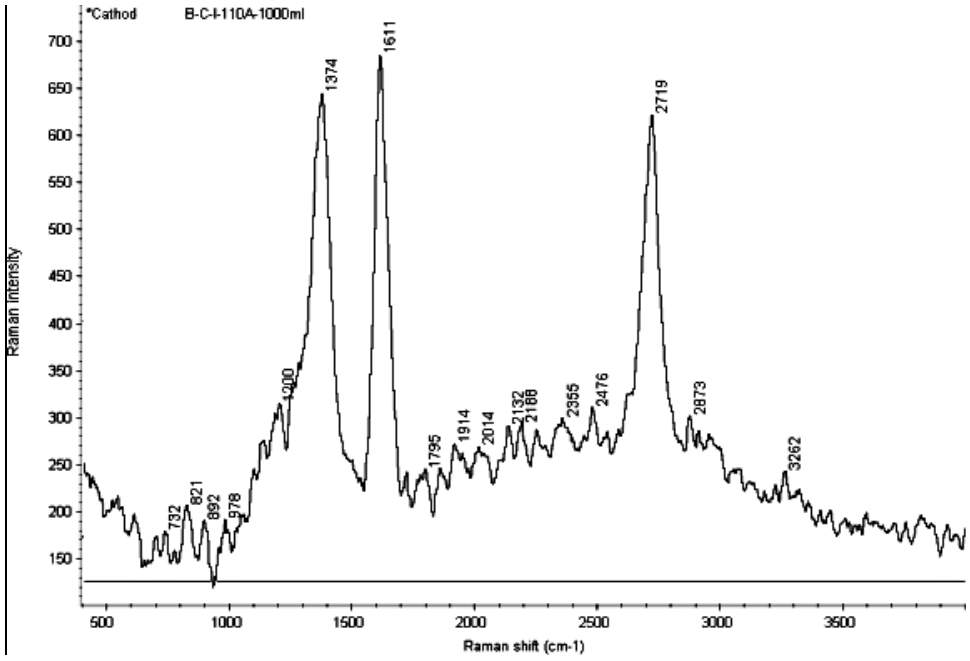

Fig. 4. Raman spectra observed from boron doped CNTs at DC current 110 A

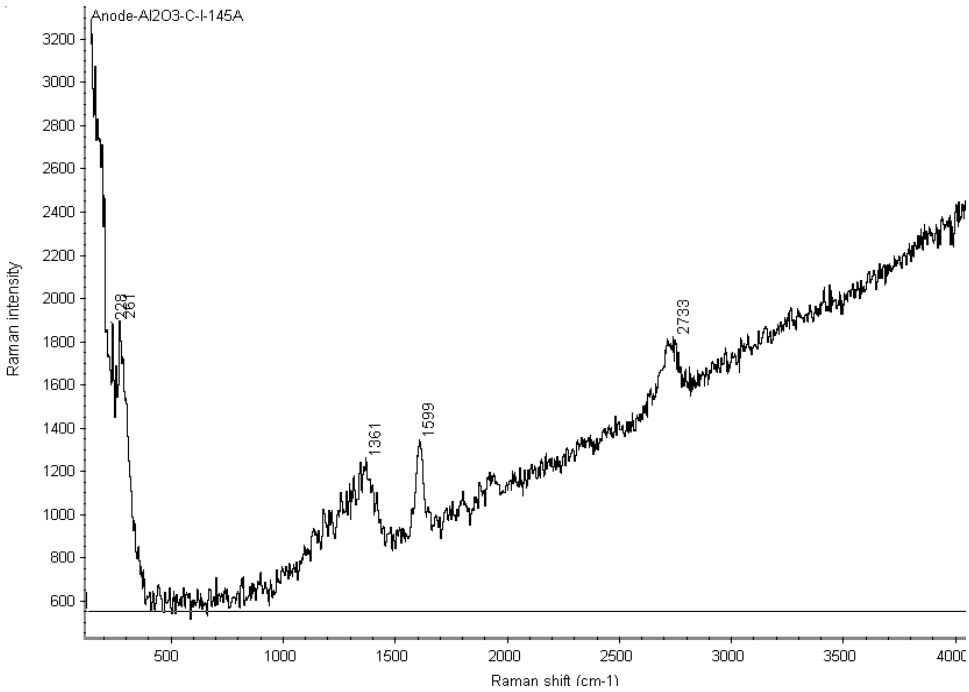

Fig. 5. Raman spectra observed from nitrogen doped CNTs at DC current 145 A with Al_2O_3 as catalyst

The Full-Width Half-Maximum (FWHM)of G-mode was calculated with this method[25];

$$FWHM = 2.35\delta \qquad \delta = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \bar{x})^2}$$

$$x_1 = 1550 \text{ cm}^{-1}$$

$$x_2 = 1690 \text{ cm}^{-1}$$

$$\bar{x} = 1620 \text{ cm}^{-1}$$

$$\delta = \sqrt{\frac{1}{2}(1550 - 1620)^2 + (1690 - 1620)^2}$$

$$FWHM = 164.5 \text{ cm}^{-1}$$

(x_1 and x_2 are the coordinates of two points in half of high maximum of mode). In comparison with (FWHM) of G-mode of non doped CNTs (20-23 cm^{-1})[14] the measure of FWHM of boron doped CNTs was increased and shows that the present experiment is right.

Figs. 5 and 6 show the Raman spectra of nitrogen doped CNTs produced by Al_2O_3 and MgO as catalysts, respectively. In both of these figures the frequencies of G-modes (1599 cm^{-1}) with Al_2O_3 as catalyst and (1592 cm^{-1}) with MgO as catalyst were decreased and the frequencies of D-modes (1361 cm^{-1}) with Al_2O_3 as catalyst and (1352 cm^{-1}) with MgO as catalyst were increased in comparison with non doped CNTs. In Fig. 4 the diameter of CNTs by using $\omega_{RBM} = 248/d_t$ cm^{-1} was calculated that approximately to get d = 1.28. Using $d = \sqrt{3}a_{c\text{-}c}\sqrt{N}\,\pi^{-1}$, $a_{c\text{-}c} = 1.42$ Å and $N^2 = n_1^2 + n_2^2 + n_1n_2$ to get $n_1 = n_2 = 1$ and the CNTs is armchair and metallic[26-28].

In Figs. 4-6, the spectra of boron and nitrogen doped produced CNTs in laboratory are shown. As clearly can be seen from the Raman spectra the B doped Raman modes shift to higher wave-numbers, whereas the CNTs doped by donor reagents[10,11] such as N were found to shift to lower wave-numbers.

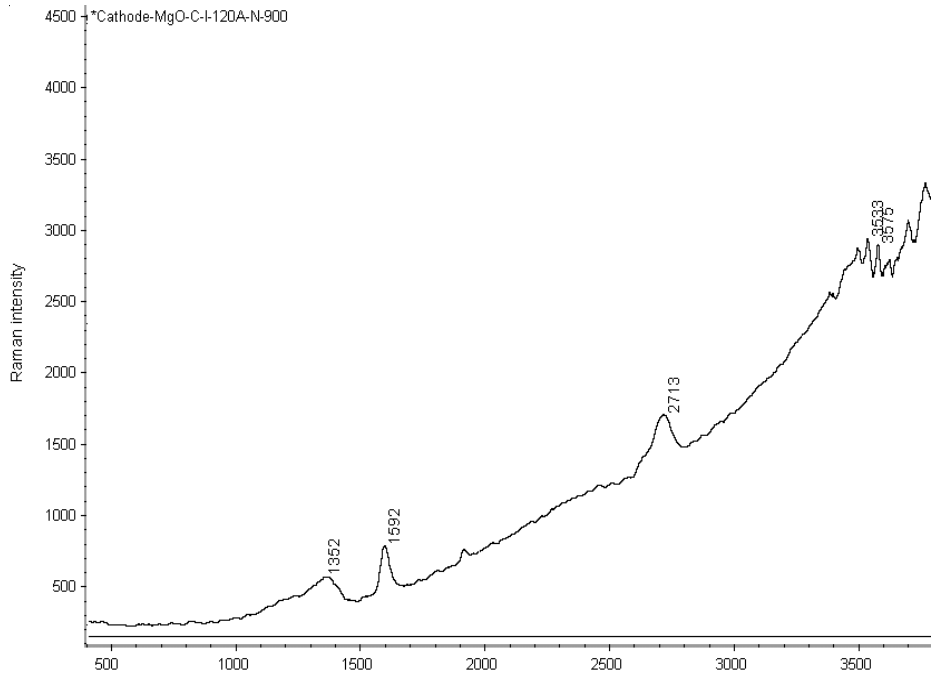

Fig. 6. Raman spectra observed from nitrogen doped CNTs at DC current 120A with MgO as catalyst

In the former case, the related N dopants act as an electron donor. The extra electron tends to weaken the C-C bond in the CNTs because electrons have been known to soften the C-C bond in all sp^2-bonded carbon material. The results of weakened bond are a downshift in tangential band to lower frequencies. However, in the case of boron doping, Raman spectra of the intercalated carbon nanotubes show opposite behaviour and towards the higher wave-numbers and the dopants are expected to act as an electron acceptor[10,11].

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