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Dispersive Micro Raman Backscattering Spectroscopy Investigation of Arc Discharge Synthesized CNTs Doped by Boron and Nitrogen

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

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1. Introduction

Elemental carbon 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 to be discovered was the fullerene molecule C_{60} by Kroto et al. [1]. Although various carbon cages were studied, it was only in 1991 when 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 (MWCNTs) with adjacent shell separation of ≈ 0.34 nm, diameters of ≈ 1 nm and large length/diameter ratio. Two years later Iijima and Ichihashi [3] and Bethune et al. [4] synthesized single-walled carbon nanotubes (SWCNTs). Nowadays MWCNTs and SWCNTs are produced mainly by three techniques: arc-discharge, laser-ablation, and catalytic growth. The synthesized nanotube samples are characterized by means of the 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 [5–9].

Among the analytical methods, the Raman spectroscopy is a powerful tool for characterizing the unique optical properties of carbon nanotubes. The Raman scattering reveals structural and unusual electronic, phonon properties, 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 superconducting 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 we have investigated the synthesized samples by this method and using the dispersive Raman backscattering spectroscopy.

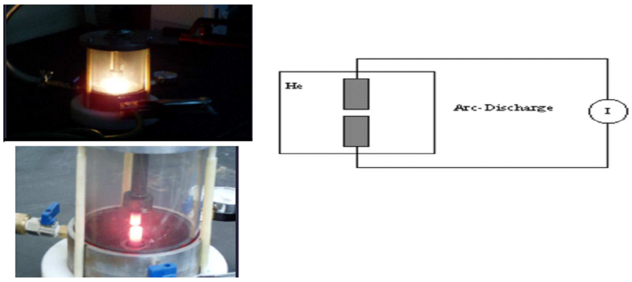

Fig. 1. The schematic representation of apparatus used in this research to produce CNTs samples.

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2. Characteristics of Raman spectra of CNTs

Figure 2 shows a typical backscattering Raman spectrum of a SWCNT synthesized in this laboratory by chemical vapor deposition method. Basically, the most characteristic 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 corresponds to the coherent vibration of the C atoms in the radial direction [16, 17] as if the tube is "breathing", and whose frequency ω_{RBM} is about 100–500 cm^{-1}. This frequency is proportional to the nanotubes diameters and is expressed as $\omega_{\mathrm{RBM}} = 248/d\ \mathrm{cm}^{-1}$ [18, 19].

2) A band at higher frequency called as disordered induced D mode which is observed at around 1350 cm^{-1} [20, 21].

3) A peak, called G mode, observed at about 1600 cm^{-1}, usually divided to two peaks or bands at higher frequencies which is related to the atomic vibrations along the circumferential direction and along their axis direction, respectively, which are called G^{+} and G^{-} modes and are seen both in semiconductor and metallic tubes [12, 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 at about 2450 cm^{-1} [23, 24].

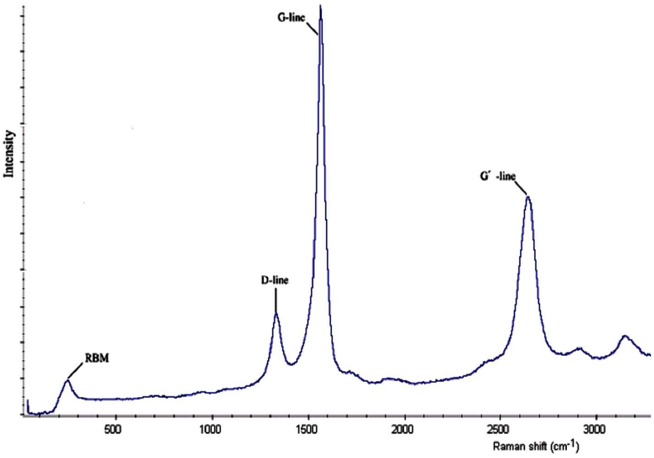

Fig. 2. Characteristic Raman peaks of pure and non-doped CNTs recorded in this research.

In our 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 experiments without using the catalysts 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, N_2 gas were used for producing nitrogen doped CNTs.

3. Doping effects

Boron and nitrogen are the nearest elements to carbon in the periodic table. Doping of graphite with such elements will modify the electronical, mechanical and oxidative properties of these materials. This offers 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. Such effects are respectively expected to behave as an acceptor (p-type) or a donor (n-type) dopants and enhance CNTs conductivity [10, 11].

4. Experimental procedures

The doped carbon nanotubes samples 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 our experiments and for producing boron doped carbon nanotubes, Ar atmosphere and graphite powder as the carbon source were used, 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 A in a gas flow of 20 sccm (standard cubic centimeter per minute) of Ar were employed. The dark grey filamentous material deposited on the cathode electrode was collected and 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 and 145 A in a gas flow of 1000 ml/min of N_2 were employed. Similarly to the first stage, the samples in this stage were collected and purified.

In the next stage and for producing nitrogen doped carbon nanotubes, MgO as catalyst at N_2 atmosphere was used. The related molecular weight of MgO and C was 3% MgO and 97% C in ethanol alcohol suspension in which DC currents of 110, 120 and 130 A in a gas flow of 1000 ml/min of N_2 were employed. The samples after collection were purified with acid and furnace heating.

The samples produced in every stage after purification were used for the Raman spectroscopy. A typical collection of the collected spectra is shown in Figs. 3–5.

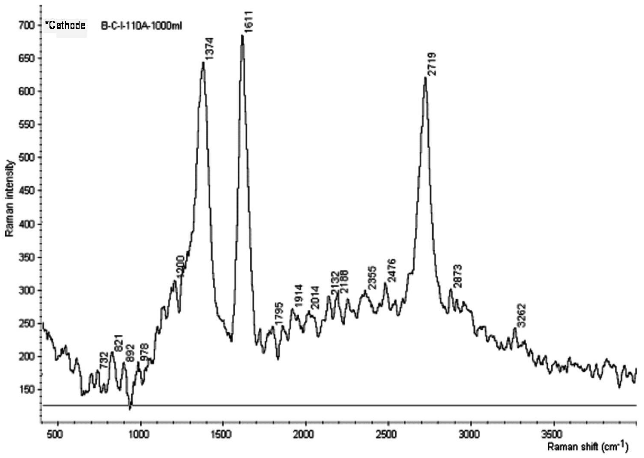

Fig. 3. A typical Raman spectrum observed from boron doped CNTs at 110 A DC current.

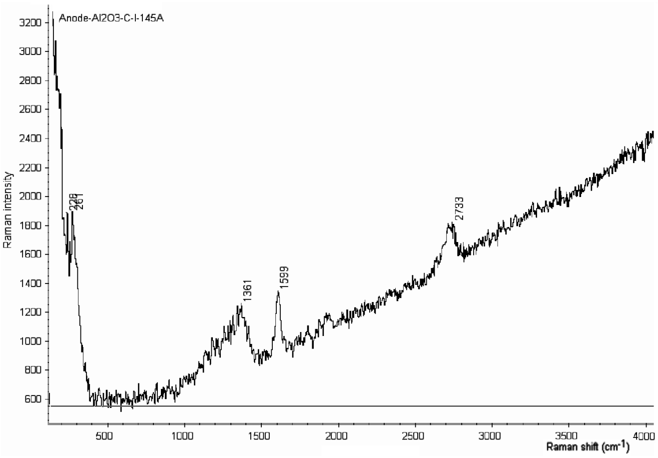

Fig. 4. The Raman spectrum observed from nitrogen doped CNTs at 145 A DC current synthesized with Al_2O_3 as catalyst.

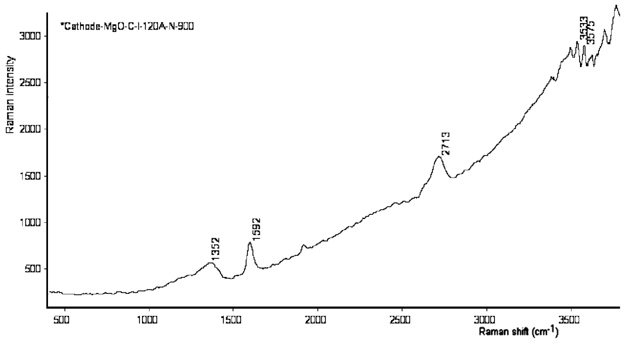

Fig. 5. The Raman spectrum observed from nitrogen doped CNTs at 120 A DC current synthesized with MgO as catalyst.

5. Results and discussions

In Fig. 3 the Raman spectrum of boron doped CNTs in the absence of catalyst at Ar atmosphere has been presented. The G-mode and D-mode frequencies are at 1611 and 1374 cm^{-1}, respectively. These Raman active modes have increased in frequencies in comparison with G-mode and D-mode frequencies of the non-doped CNTs which are at 1600 and 1350 cm^{-1}, respectively [10, 22].

The reasons of increasing the G-mode and D-mode frequencies can be summarized as follows:

The boron atoms can capture additional electrons from neighboring carbon atoms (as acceptor) which causes strengthening the bond of B–C. Accordingly, the G-mode frequency shifts to higher frequencies.

The increase of D-mode frequency causes increase in the disorder of the CNTs structure.

In Fig. 3 the existence of several RBM-modes shows that the synthesized CNTs is MWCNTs whereas in Fig. 5 existence of two RBM-modes shows that the produced CNTs is double wall CNTs.

The full-width at half-maximum (FWHM) of the G-mode can be calculated with the following formula [25]:

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

$$x_1 = 1550\ \text{cm}^{-1},\ x_2 = 1690\ \text{cm}^{-1},\ \bar{x} = 1620\ \text{cm}^{-1},$$

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

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

(x_1 and x_2 are the wave number positions of the 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 has increased and confirms the procedure of our experiment.

Figures 4 and 5 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 the G-modes at 1599 cm^{-1} with Al_2O_3 as catalyst and 1592 cm^{-1} with MgO as catalyst were decreased. However, the frequencies of D-mode at 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. 3 the diameter of CNTs by using the empirical formula $\omega_{\text{RBM}} = 248/d\ \text{cm}^{-1}$ was calculated which approximately leads to $d = 1.28$ nm. We used $d = \sqrt{3}a_{\text{C-C}}\sqrt{N}\pi^{-1}$, $a_{\text{C–C}} = 1.42$ A and $N^2 = n_1^2 + n_2^2 + n_1 n_2$ to get $n_1 = n_2 = 1$ and the CNTs is armchair and metallic forms [26–28].

In Figs. 3, 4 and 5 the spectra of boron and nitrogen doped produced CNTs in our laboratory are shown. As clearly can be seen from the Raman spectra, the B doped Raman modes shift to the higher wave numbers, whereas the CNTs doped by donor reagents [10, 11] doped samples were found to shift to the lower wave numbers.

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, the Raman spectra of the intercalated carbon nanotubes show opposite behavior and towards the higher wave numbers and the dopants are expected to act as an electron acceptor [10, 11].

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