SYNTHESIS AND PHOTOLUMINESCENT PROPERTIES OF IODINATED MULTI WALLED CARBON NANOTUBES

S. H. ABDULLAYEVA[1,2], S.A. MAMMADOVA[1], A.B. HUSEYNOV[2], A.O. ISRAFILOV[2]

1. Institute of Physics named after G. M. Abdullayev, Azerbaijan National Academy of Sciences

2. High Tech Research Center under the Ministry of Transport, Communications and High Technologies of the Republic of Azerbaijan

samiras416@gmail.com

This paper reports synthesis and photoluminescent properties of iodinated multi-walled carbon nanotubes (I-MWCNTs). MWCNTs were synthesized by Aerosol-Chemical Vapor Deposition method (A-CVD) and iodinated by crystalline iodine under increased pressure (approximately∽ 20 bar) at 400^0 C. X-Ray Diffraction (XRD) and Raman spectroscopy aanalysis proved the presence of iodine atoms in I-MWCNTs. After iodination, the concentration of introduced iodine atoms constitute approximately 30% in weight. Photoluminescence (PL) intensity of the I-MWCNTs remarkably enhanced by the introduction of iodine atoms and explained with defects, due to the formed covalent C - I bonds over the MWCNTs which can play the role of luminescence centres in I- MWCNTs. I-MWCNTs show a wide emission spectrum with two emission peaks (430nm, 520nm). For the first time the intensity of these peaks was highly increased due to the effective iodination of MWCNTs by our group.

Keywords: A-CVD, Iodinated Multi Walled Carbon Nanotubes, Photoluminescence, XRD, Raman spectroscopy
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1. INTRODUCTION.

The visible luminescence of the functionalized carbon nanotubes in solution firstly discovered by Riggs [1]. Later, this was confirmed by another studies in literature [2-4]. The low toxicity and photoluminescent properties of carbon nanotubes makes this material very useful in the field of photonics and for large scale optoelectronic applications. Only a few studies have investigated the photoluminescent properties of iodinated MWCNTs [5-7]. This motivated us to prepare I-MWCNTs and investigate their photoluminescent properties.

2. EXPERIMENTAL SECTION

Pristine MWCNTs were synthesized by an Aerosol - Chemical Vapor Deposition method (A-CVD) on the experimental laboratory setup (Scientific Instruments Dresden GMBH, SCIDRE, Germany). Cyclohexane (Cy) was used as a source of carbon and ferrocene (Fc) as a catalyst precursor [8]. Synthesis process was carried out at 9000C temperature at atmospheric pressure.

Iodination of MWCNTs were prepared in a sealed quartz ampoule under increased pressure (approximately ~ 20 bar) at 400°C for 2 hours. The obtained product was washed in ethanol until the absorbed iodine completely disappeared and dried at 120 °C temperature.

The iodinated MWCNTs were characterized by Raman spectroscopy and XRD. Raman scattering measurements were performed in a wide wavenumber range between 500 and 9000 cm^{-1} by Nanofinder 30 Confocal Laser Microspectrometer method operating at 532 nm laser line (Laser power 8mW, a 100 grooves/mm grating, exposure time 10s).

X-ray diffraction patterns were recorded using a Bruker 5000 diffractometer in standard (θ-2θ) geometry using Cu Kα radiation.

Photoluminescence (PL) measurements of I-MWCNTs / ethanol suspension in the 350-700 nm regions were obtained upon excitation with the 325 nm lines of an IK series He-Cd laser.

3. RESULTS AND DISCUSSIONS

3.1 X-RAY DIFFRACTION ANALYSIS

XRD studies were performed on iodinated MWCNTs and shown in Fig. 1. It is clear from the XRD analysis that the main peaks at 26 ^{0} (002), 43^0 (100) and 53.2^0 (004) shows good consistence to the data from the standard CNTs diffraction file (PDF 00-058-1638) and proves high crystallinity of MWCNTs.

Moreover, XRD spectra proves the presence of covalent C- I bonds over the carbon nanotubes and small amount of absorbed iodine atoms into the pores of MWCNTs.

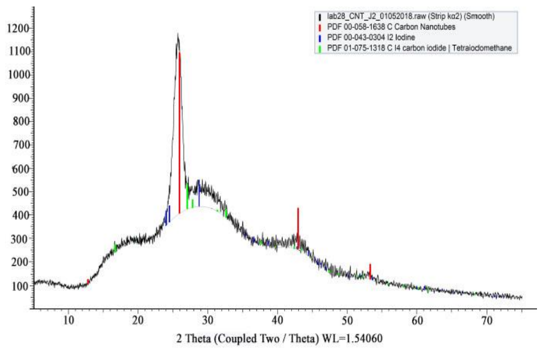

Fig.1. XRD patterns of pristine and I- MWCNTs

3.2 RAMAN SPECTROSCOPY

Raman spectra of both, pristine and I-MWCNTs were recorded using 532 nm exciting line. The Raman spectra of pristine and I-MWCNTs exhibits similar characteristic peaks (fig.2).

131 H.Javid ave, AZ-1143, Baku
ANAS, G.M.Abdullayev Insttute of Physics
E-mail: jophphysics@gmail.com

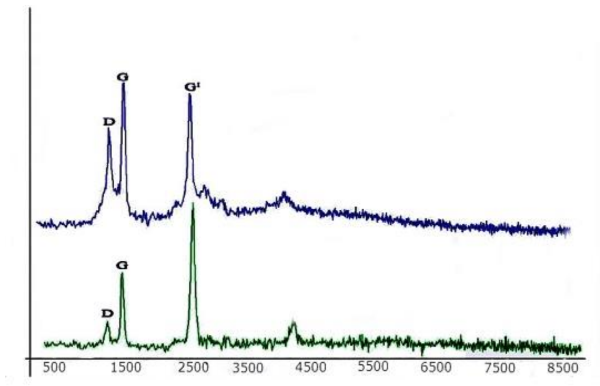

Fig.2. Raman spectra of pristine MWCNTs (green line) and I - MWCNTs (blue line)

The main exception is that for I-MWCNTs the D band intensity at approximately ($1300 cm^{-1}$) significantly increases compared to the pristine MWCNTs. After iodination, a large number of C-I bonds were formed over the MWCNTs surface, due to the interaction large amount of iodine atoms (30% wt). The increase of the D/G ratio implies that more sp^2-hybridized carbons are converted to sp^3 - hybridized carbons and form defects. It is assumed that these defects play the role of luminescent centers.

3.3. UV-VIS PHOTOLUMINESCENCE PROPERTIES OF IODINATED MWCNTS

Photoluminescence emission spectra of the pristine and I-MWCNTs suspension in ethanol are reported in Fig. 3. Experiments were carried out with the 325 nm laser excitation of samples in the 300-700 nm region. As shown in Fig. 3, I-MWCNTs have a wide emission spectrum with two emission peaks (430nm, 520nm).

The enhancement of peaks can be explained with distribution of nonequivalent emission sites due to the dispersion of the defects with iodination of MWCNTs. The C-I bonds can form defects which can play the role of luminescent centers in I- MWCNTs.

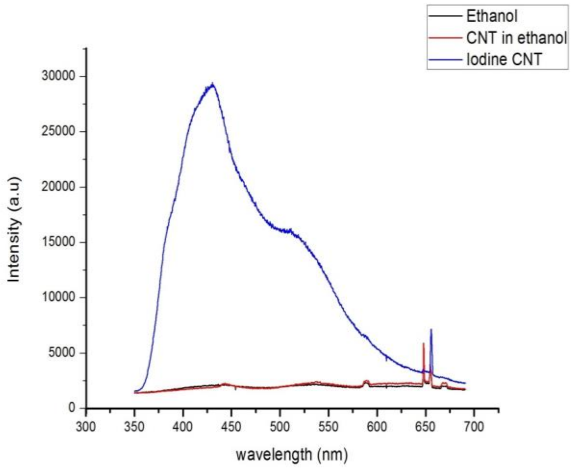

Fig. 3. Photoluminescence (PL) spectra of ethanol (black line), pristine MWCNT /ethanol (red line) and I-MWCNTs /ethanol (blue line) suspension

CONCLUSIONS

MWCNTs were synthesized by A-CVD method at 900^0 C and iodinated with a simple chemical route in a sealed quartz ampoule at 400 °C for 3 hours. In comparison with other authors, our group firstly obtained functionalized carbon nanotubes with iodine content of 30 wt%. XRD analysis have shown the presence of iodine phases on spectrum and Raman spectroscopy revealed the enhancement of defect band in iodinated MWCNTs. I-MWCNTs suspension in ethanol exhibits emission spectrum with two intense peaks at blue (430 nm) and green (520 nm) regions. For the first time the intensity of these peaks was highly increased which is explained with defects that formed due to the C-I chemical covalent bonds (which play the role of luminescent centers for I-MWCNTs) after incorporation of iodine atoms.

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