HIGH QUALITY AND RELIABLE CARBON NANO-STRUCTURES USED FOR 3rd GENERATION OF SOLAR CELLS

Dorel DOROBANTU, Petru-Marian BOTA, Matei BADEA, Iulian BOERASU, Dionezie BOJIN, Marius ENACHESCU

Centre for Surface Science and Nanotechnology, Politehnica University of Bucharest, Splaiul Independentei 313, Bucharest, ROMANIA; e-mail: marius.enachescu@upb.ro

Abstract. The synthesis of high-quality single-walled carbon nanotubes (SWCNTs) in a new laser ablation chamber design for Kr-F excimer laser depositions is reported. The average external diameter of SWCNTs ranging from 1.2nm to 1.4nm were found by TEM analysis and confirmed by micro-Raman spectroscopy. The optoelectronic properties of the SWCNTs-poly(3-octilthiophene) (P3OT) composite are reported. A value of about 2.4eV was estimated for the SWCNTs-P3OT optical band-gap from optical measurements at room temperature. These results show that the synthetized SWCNTs are suitable for integration in fabrication of the 3rd generation of solar cells.

Keywords: laser ablation, single-walled carbon nanotubes, 3rd generation solar cells, SWCNTs chemical purification

1. Introduction

Single-walled carbon nanotubes (SWCNTs) have been of great interest in the last years due to their potential implementation on Key Enabling Technologies (KETs) such as nanotechnology, micro- and nano-electronics including semiconductors, advanced materials, biotechnology and photonics [1]. Areas where the carbon nanotube properties appear to have real marketable applications in the near future are energy and biology. Disruptive breakthroughs on SWCNTs fabrication are required to develop a large-scale market for these applications. A critical element for SWCNTs implementation is to mastering the fabrication of high quality, reliable and in high yield of SWCNTs. A variety of techniques were reported by the literature for fabrication of SWCNTs [2], but pulse laser vaporization (PLV) stands out by its capacity to produce exclusively SWCNTs at the highest yield ever reported (~80%) [3]. In this work, the successful fabrication of SWCNTs by means of UV laser vaporization is reported. The performances and promising integration of produced SWCNTs in 3rd generation of photovoltaic devices is also highlighted.

2. Experimental

Laser-assisted SWCNTs formation has been performed in a novel custom designed laser ablation chamber for UV laser vaporization experiments. A picture of the experimental set-up is presented in Figure 1. Complete technical details about the novelty of the used ablation chamber are reported elsewhere, together with obtained progress beyond state-of-the-art [4].

SWCNTs were produced by ablating a Co/Ni-doped graphite target by means of a Compex Pro 205 (Coherent) pulsed KrF excimer laser (wavelength 248 nm; pulse length 25ns; repetition rate of 30Hz and laser intensity 3:5 x 10^8 W/cm^2).

The laser beam was focused on a 20mm^2 spot perpendicularly to the target surface. In order to ensure a uniform target surface ablation, the target was rotated during ablation.

The graphite target was fabricated by a novel preparation route, by adding Co/Ni (with 0.6 at% Co and 0.6 at% Ni) catalyst powders to a carbon adhesive, Graphite Cement GC-8010B (supplied by Metal Forming Lubricants, Inc.). The novelty of the target preparation, elsewhere reported and in details discussed [4], consists in that the carbon adhesive was used as the unique graphite precursor. Another novelty in our preparation recipe consists in that no pressing or hot-pressing procedures were employed for target preparation.

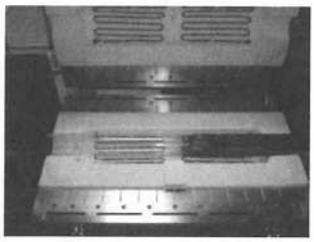

FIGURE 1: General view of the new laser ablation chamber design for Kr-F excimer laser.

The as-grown SWCNTs were purified by applying acid digestion method [5] in order to eliminate the metallic catalyst nanoparticles. Purification was consisting in 16-h reflux in 3M nitric acid (60mL of acid per 80mg of raw material) at 130 ^{0}C.

Following the reflux the black solution was filtered using PTF membrane filter with pore size 200 nm, and the filtrate was in abundance washed with distilled water.

Un-purified and purified SWCNTs were added to distilled water and then introduced in an ultrasonic bath to disperse the nanoparticles for 15 minutes. Using a thin glass dropper a droplet was collected from the solution and studied by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) using a JEOL-ARM200F TEM equipment. Raman spectroscopy of both un-purified and purified ablation products was performed using a Horiba LabRam 800 with an excitation wavelength of 532 nm, in the spectral range 100 – 2500cm^{-1}.

Preparation of the SWCNTs–P3OT composite solutions was performed using a series of mixing and sonication steps. The necessary amount of regioregular P3OT (Aldrich) was dissolved in chloroform using ultrasonication to achieve the pristine 15 mg/ml solution. Composite dispersion was performed by combining the appropriate mass of purified SWCNTs to the pristine solution at desired doping levels. The final solution was

deposited on a 2.5x2.5 cm^2 ITO-glass substrate by drop cast and spin coating technique (1500rpm/60s at room temperature). To complete the solar cell fabrication, aluminium contacts was applied to the SWCNT–P3OT composite film layers by thermal evaporation under vacuum with a standard shadow mask.

Optical absorption was determined using a combination of UV-visible transmission and reflection spectra measured with a UniCam UV2 UV/VIS spectrophotometer.

TheI–V characteristics were monitored using a Keithley 237 source measurement unit.

3. Results and discussions

The TEM images of the resulted products by laser ablation of Co/Ni doped graphite target are shown in Figure 2.

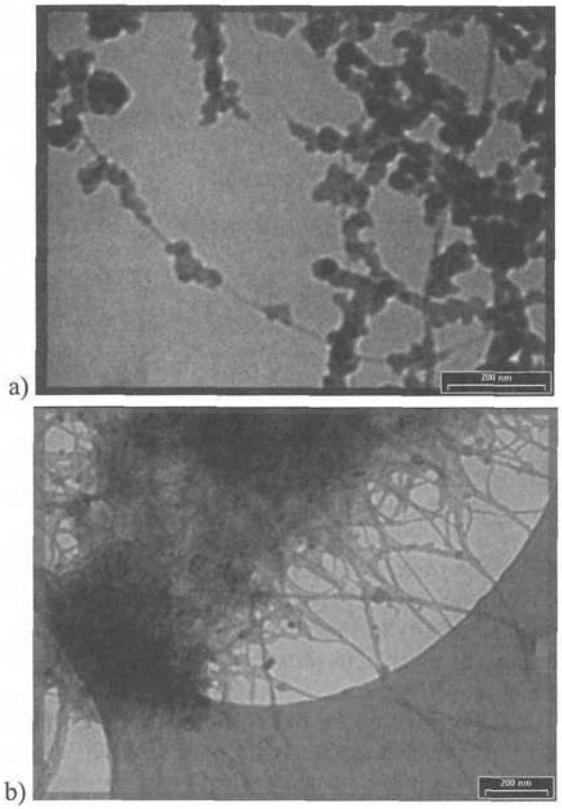

FIGURE 2: TEM images of the ablation products a) un-purified and b) purified.

The raw ablated products (un-purified) look like well-defined SWCNTs individually or grouped into bundles (see Figure 2a)). The estimated diameter values of singular observed SWCNTs ranged between 1.2 nm and 1.4 nm. The as-produced SWCNTs contain two types of impurities: transition metal catalyst particles (typically Co and Ni) and carbonaceous species, which include amorphous carbon, fullerenes, multi-shell carbon nano-capsules, and nano-crystalline graphite. A representative TEM image of the ablated products after purification step is shown in Figure 2b). It can be seen that all most of the catalyst particles have been removed. Moreover, a notable quantity of carbonaceous species is observed on recorded pictures. In order to remove this carbonaceous species, further thermal oxidation treatments should be performing on the as chemical purified samples [5].

In Figure 3 the Raman spectra of the un-purified and purified SWCNTs are shown.

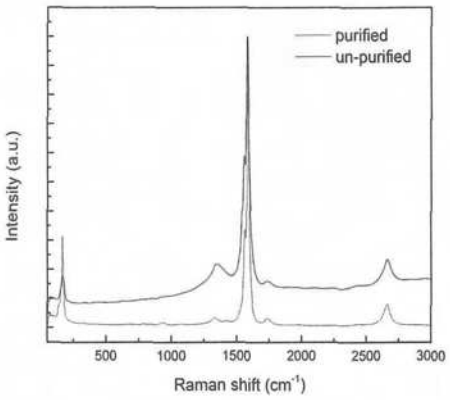

FIGURE 3: Raman spectra of un-purified and purified SWCNTs obtained by UV laser vaporization.

At low frequencies using the 532nm wavelength shows characteristic maximums at 150 cm^{-1}, 156 cm^{-1}, 160 cm^{-1} and 165 cm^{-1}.

At high frequency, strong features centred at 1340 cm^{-1} and 1585 cm^{-1}, could be observed. These features are ascribed to D-band and G-band of carbon nanotubes. The G band is an indication of the graphitic quality of the sample while the D band is normally taken as an indication of degree of disorder. The full-width-half-maxima (FWHM) of the D band are an indication of the amount of carbonaceous impurities. The sample quality (defect density) can be checked by comparing the D to G band Raman intensity. The D to G peak intensity ratio drops by a factor of about four on purification, while the D peak FWHM drops by 40%, confirming the improved purity after treatment. This behaviour in the peak intensity is quite typical for acid treated tubes in which the peak originating from metallic tubes decreases when the tubes are acid treated due to a loss of continuum states as a result of functionalization of the tubes compared to the raw tubes [6].

At low frequencies using the 532nm wavelength shows characteristic maximums at 150 cm^{-1}, 156 cm^{-1}, 160 cm^{-1} and 165 cm^{-1}. Using the well-known equation [7]:

$$\omega_{RBM} = \frac{c_1}{d} + c_2 \qquad \text{Eq.1}$$

where w_{RBM} is the radial breathing mode frequency (in cm^{-1}), c_1=215cm^{-1} and c_2=18cm^{-1} are constants, the diameter d of the SWCNT (in nm) could be estimated. The estimated values are ranging from 1.2nm to 1.3nm. The as obtained values are in good agreement with the estimated tube diameter by TEM technique.

For SWCNTs integration on 3rd generation of solar cells, blends of SWCNTs with conjugated polymer, poly(3-octylthiophene), has been performed.

The optical absorption spectrum, deduced from transmission-reflectance measurements is presented in Figure 4. The optical band gap ($E_{g\,OPT}$) of the composite is estimated at around 2.4 eV in very good agreement with the values reported by the literature [8].

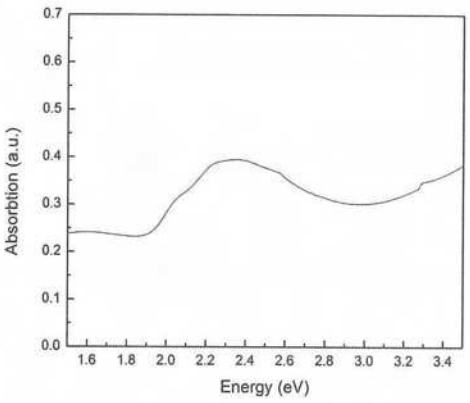

FIGURE 4: Optical absorption spectra of the SWCNT-P3OT composites deposited on ITO-glass by spin-coating.

Considering the reported value of highest occupied molecular orbital (*HOMO*) for P3OT to be 5.4 eV, we calculate the value of lowest unoccupied molecular orbital (*LUMO*) according to the equation [8]:

$$LUMO=HUMO - E_{g\,OPT} \qquad \text{Eq.2}$$

The as obtained value of about 3eV is in good agreement with those reported in literature [9] proving the quality of prepared structures.

The logarithmic current density (J) versus the voltage (V) of the P3OT-SWCNT based photovoltaic cell in dark and under light is plotted in Figure 5.

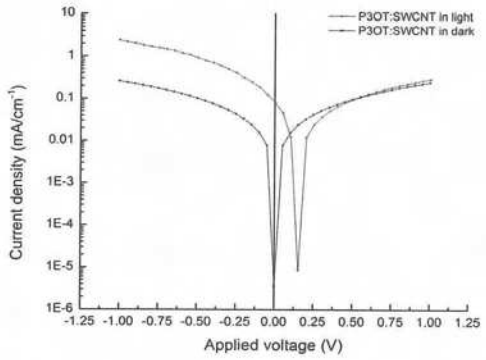

FIGURE 5: I–V characteristics of an Al/P3OT-SWCNT/ ITO/glass device measured in the dark and under illumination as a logarithmic plot.

The as recorded current density JSC in light of 0.09mA/cm^2 is in good agreement with values reported by other teams [9]. However, even if the current density fits the reported values, its magnitude is slightly higher for higher values of applied voltages. This behaviour could be related with the leakage currents of high magnitude in the measured structures. It is reported by the literature that the leakage current is caused by the current through local defects in the organic hetero-junction or due to the shunts at the edges of solar cells [11]. In our case, the magnitude of the leakage currents is more related with local defects induced into the organic hetero-junction by the presence of the residual metallic catalysts used during the laser ablation synthesis, also observed on TEM images. Further purification experiments are in progress in order to establish the optimal parameters for a complete digestion of metals by chemical attack. Thus, a drop of the leakage current is expected.

4. Conclusions

SWCNTs were successful synthetized in a novel custom design ablation chamber. The high quality of produced SWCNTs was proved by careful morphological analysis. The TEM and HR-TEM recorded imagines shown that the obtained SWCNTs has a diameter ranging from 1.2 to 1.4 nm, values confirmed also by micro-Raman spectroscopy analysis. The produced Mixtures of Co/Ni catalysts were used for preparing the ablated targets following a new preparation technique. The influence of an acid digestion of metallic catalysts on the ablation products was pointed out by means of TEM and Raman analysis. Results about the optical and electrical measurements make evident the promising integration of SWCNTs on the fabrication of the 3rd generation of solar cells.

Acknowledgments

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References

[1] Enachescu M., *Market Watch* 150, 34, 2012

[2] Guo T., Nikolaev P., Thess A., Colbert D.T., Smalley R.E., *Chemical Physic Letters* 243, 49, 1995.

[3] Thess A., Lee R., Nikolaev P., Dai H., Petit P., Robert J., Xu C., Lee Y.H., Kim S.G., Rinzler A.G., Colbert D.T., Scuseria G.E., Tom D., Fischer J.E., Smalley R.E., *Science* 273, 483, 1996.

[4] Bota P. M., D., Boerasu I., Bojin D., Dorobantu D, Enachescu M., *Submitted to Review of Scientific Instruments*, 2013.

[5] Landi B. J., Raffaelle R. P., Castro S. L., Bailey S. G., *Progress in Photovoltaic: Research and Applications* 13, 165, 2005.

[6] Duesberg G.S., Roth S., Downes P., Minett A., Graupner R., Ley L., Nicoloso N., *Chemical Materials* 15, 3314, 2003.

[7] Maultzch J., Teig H., Reich S., Thomsen C., *Physical Review Letterers B* 70, 155403, 2004.

[8] Mwaura J. K., Pinto M. R., Witker D, Ananthakrishnan N., Schanze K. S., Reynolds J. R., *Langmuir* 21, 10119, 2005.

[9] Kymakis E., Amaratunga G. A., *Applied Physic Letterers* 80 112, 2002.

[10] Krüger M., Buitelaar M. R., Nussbaumer T., Schönenberger C., Forro L., *Applied Physic Letterers* 78 1291, 2001.

[11] S. Dongaonkar, J. D. Servaites, G. M. Ford,3 S. Loser, J. Moore, R. M. Gelfand, H. Mohseni, H. W. Hillhouse, R. Agrawal, M. A. Ratner, T. J. Marks,

M. S. Lundstrom, M. A. Alam, *Journal of Applied Physics* 108, 124509, 2010