

TUNING CARBON NANOTUBES FOR APPLICATION IN SOLAR CELLS

Zivayi Chiguvare², George Bepete^{1,2}, and Neil J. Coville¹

¹DST/NRF Centre of Excellence in Strong Materials and Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, Johannesburg 2050, (South Africa)

² DST/NRF Centre of Excellence in Strong Materials and Material Physics Research Institute, School of Physics, University of the Witwatersrand, Private Bag 3, Johannesburg 2050, (South Africa)

1. Abstract

We achieved the control of diameter, length and level of nitrogen doping in synthesis of nitrogen doped carbon nanotubes (N-CNTs) through careful selection of catalyst, precursor mixture, and chemical vapor deposition (CVD) synthesis temperature. Solutions of butanol and acetonitrile (20% acetonitrile) were pyrolysed over a Fe/Al/MgO catalyst in a CVD reactor at temperatures from 700 °C to 1000 °C. The products were characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and Raman spectroscopy. N-CNTs with well graphitized morphology, small diameter, and narrow diameter distribution were obtained at CVD temperatures from 850 °C to 950 °C. Below 800 °C N-CNTs with large sized diameters were formed and above 950 °C the product yield became very low, and the carbon nanotubes were malformed with wide diameter distributions. By pyrolysing precursor mixtures of acetonitrile and alcohols (methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol and octanol) we found out that short, 500 nm in length, N-CNTs were obtained by the pyrolysis of long chain alcohols, (heptanol and octanol) and acetonitrile solution whilst longer N-CNTs were formed from pyrolysis of shorter chain alcohols (methanol, ethanol and propanol).

2. Introduction

Polymer based photovoltaic devices can be made using a coating process such as spin coating or inkjet printing, hence they are an attractive option for inexpensively covering large areas of flexible plastic surfaces. Efforts to incorporate carbon nanotubes (CNTs) in organic solar cells have not yet yielded the requisite efficiencies for such cells to be competitive economically. Using CNTs the best power conversions achieved to date were obtained by depositing a single wall CNT layer between indium tin oxide (ITO) and the poly (ethylene dioxythiophene) doped with polystyrene sulfonate (PEDOT : PSS) or between the PEDOT: PSS and the photoactive blend in a modified ITO/PEDOT: PSS/ poly(3hexyl)thiophene : (6,6)-phenyl-C₆₁-butyric acid methyl ester (PCBM)/Al solar cell. By dip-coating from a hydrophilic suspension, SWCNTs were deposited after initially exposing the surface to an argon plasma to achieve a power conversion efficiency of 4.9%, compared to 4% without CNTs (Chaudhary *et al.*, 2007).

The chemical bonding of CNTs is composed entirely of sp² bonds, similar to those of graphite. This bonding structure, which is stronger than the sp³ bonds found in diamonds, provides the molecules with their unique strength. Recent studies have shown that doping CNTs with hetero-atoms is an alternative to functionalizing CNTs and can lead to modification of length, diameter (Terrones *et al.*, 2004) and also electronic properties of CNTs. Nitrogen and boron are the most frequently used dopants because their atomic radius is similar to that of carbon and because they serve as *p*- or *n*- type dopants respectively (Terrones *et al.*, 2002). Nitrogen doped carbon nanotubes (N-CNTs) and boron doped CNT (B-CNTs) can be employed as highly selective electron- or hole-transport materials to give remarkable device performance enhancement in organic solar cells (Lee, 2011). Castrucci *et al.*, 2006 showed that multi-walled CNTs (MWCNT) are more effective than SWNTs in photocurrent generation in organic solar cells.

The role of the CNTs in the solar cells is not yet fully understood. For instance it is thought that they can enhance the charge carrier collection, in a bulk heterojunction solar cell with a polymer – fullerene active layer, e.g., P3HT: PCBM. However the efficiencies obtained to date for such types of solar cells remains below that of polymer-fullerene solar cells that have just entered commercial manufacture. The reasons for the reduction in efficiency when CNTs are incorporated include shorting between electrodes, lack of clarity on the nature of the synthesized CNTs, i.e., whether they are metallic or semiconducting, and whether they are *n*- or *p*- type.

The introduction of nitrogen to the graphene layers of the carbon nanotube takes place during synthesis and therefore the conditions used in the catalytic growth process are important. The process of N-CNT synthesis takes place in three stages: 1) decomposition of the precursor to surface carbon and nitrogen atoms, 2) diffusion/ migration of these atoms through/ over the metal, and 3) formation of the N-CNT. In order to be able to tune the physical chemical properties of the N-CNT one needs to influence one or more of the above mentioned stages.

The long term goal of this study is to contribute towards the development of a low-cost, strong and reliable, highly efficient polymer-nanocarbon solar cell. In this paper we report on the determination and optimization of the CVD conditions necessary for the synthesis of nitrogen doped carbon nanotubes of desired properties (e.g. pure, short, small diameter, soluble). We show that changes in synthesis parameters, specifically temperature, and N/C source, will affect the physical-chemical properties of the resulting N-CNTs, e.g. the graphitic character, the amount and type of nitrogen incorporated, as well as thermal stability. We also give preliminary results obtained in ITO/PEDOT:PSS/P3HT:PCBM/Al solar cell trials incorporating these N-CNTs.

3. Experimental

N-CNTs were synthesized by the catalyst chemical vapor deposition method (see Fig. 1). The catalyst employed in this work was Fe/Al/MgO with molar ratio of 1:1:12. A quartz boat with 300 mg catalyst powder was inserted in the centre of a quartz tube reactor. The reactor was heated to the required temperature in 5% H₂ in argon flow at 240 ml/min. At a steady temperature the carbon and nitrogen source (80% alcohol and 20% Acetonitrile) mixture was introduced by means of a 20 ml syringe driven by a pump at 1.2ml/min for 20 minutes. Finally the reactor was cooled to ambient temperature under the flow of 5% H₂ in argon. The alcohols employed in this case include ethanol, methanol, pentanol, butanol, and heptanol.

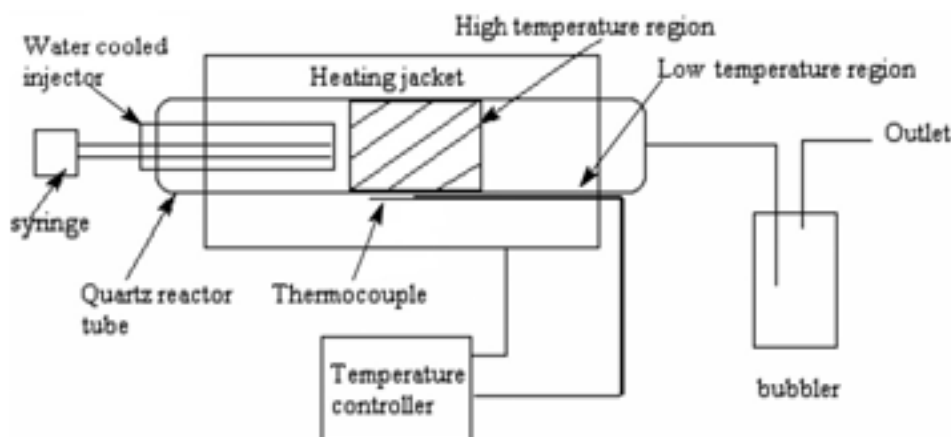


Fig. 1: Schematic of a temperature controlled CVD furnace (Coville *et al.* 2005)

Purification of N-CNTs was achieved by refluxing for 6 hours in NaOH followed by refluxing for 12 hours in 33% HCl and washing several times with distilled water and then drying for 24 hours in an oven at 100°C. They were characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy.

Photovoltaic devices were fabricated on clean patterned ITO coated glass substrates by first spin coating PEDOT:PSS, a hole transport layer, followed by a 10 mg/ml 1:1 mass % P3HT:PCBM composite solution including 1% mass N-CNTs. The Al top electrodes were deposited by thermal evaporation in high vacuum. IV characteristics were obtained under solar simulated AM1.5 spectrum white light of different intensities at room temperature using an HP 4141 source measure unit.

4. Results

Figure 2 (a) and (b) show typical TEM micrographs for the synthesized carbon nanotubes. Carbon nanotubes with bamboo structures along their whole lengths were obtained for all temperatures, and for all alcohols employed in the synthesis, suggesting successful nitrogen incorporation in the CNT structures.

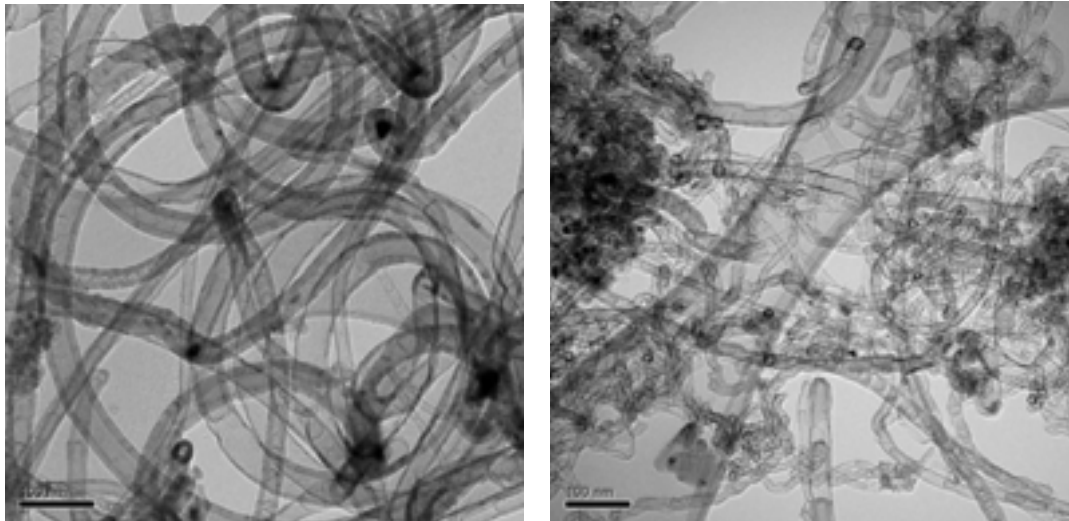


Fig. 2: TEM micrographs of CNTs synthesized at CVD temperatures (a) 750 °C and (b) 950 °C

The diameters of CNTs synthesized at 700 °C are large and approximately uniform. The average diameter is 5 nm while the length is larger than 100 μm . At 950 °C, most of the tubes have smaller diameters ~ 2 nm, but both the diameter, and the length distributions are larger.

The N-CNTs synthesized at different temperatures were studied by first order Raman spectroscopy. Two first order peaks at $1350 - 1356 \text{ cm}^{-1}$ and at $1583-1592 \text{ cm}^{-1}$ which correspond to the D and the G band respectively were observed for all the samples studied. Raman spectroscopy can be used to measure the quality or purity of the carbon nanotubes by comparing the intensity of the D band which occurs at approximately 1350 cm^{-1} to the intensity of the G band which occurs at 1582 cm^{-1} . The D-band arises from disorder or defects within the carbon nanotubes structure and also from the edges of the N-CNTs structure. The G-band arises from the sp^2 bonded carbon in the carbon nanotubes structure. An increase of N in CNT causes an increase of the I_D/I_G ratio. We also observed a decrease in the I_D/I_G ratio with an increase of synthesis temperature. We infer from Fig 3(a) that higher temperatures are conducive to more graphitic CNTs since Raman spectra indicate larger intensity for the G peak as compared to the D peak at higher temperatures.

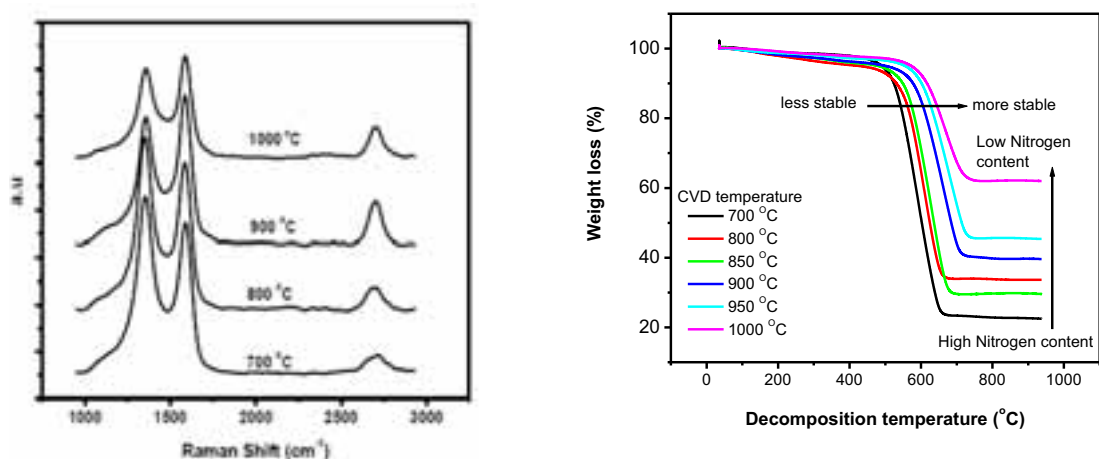


Fig. 3: (a) Raman spectra, and (b) TGA plots, for CNTs synthesized at different CVD temperatures between 750 °C and 1000°C

The TGA results (Fig. 3(b)) show that CNTs decompose at temperatures above 500 °C. The decomposition temperature increases with CVD synthesis temperature suggesting a higher thermal stability for N-CNTs synthesized at those temperatures. The amount of residue after decomposition is lower for N-CNTs synthesized at low temperatures. This is related to the purity of the CNTs. Less pure CNTs decompose at low temperatures, while purer CNTs decompose at higher temperatures. This suggests that more defects (Nitrogen) are incorporated in the CNTs when the CVD temperature is low.

We confirmed this through the XPS measurements of our N-CNTs synthesized at different CVD temperatures. An XPS plot for our N-CNTs synthesized at 850 °C is shown in Fig 4(a). Total nitrogen incorporated decreases with CVD synthesis temperature as shown in Fig. 4(b). We found that from XPS data, that quaternary nitrogen incorporation was dominant over the other forms of nitrogen incorporation at high temperatures above 800 °C.

The quantities of nitrogen species in the N-CNT samples (extracted from XPS data) are plotted against CVD synthesis temperature in Fig. 4(b). The plots are not parallel hence these quantities are not decreasing proportionally to the decrease in total nitrogen content. All the nitrogen species decrease in quantity with increase in CVD synthesis temperature, but pyridinic nitrogen and oxidized pyridinic nitrogen decrease faster (the graphs are steeper) than quaternary nitrogen. After 850 °C pyridinic and oxidized pyridinic nitrogen are not incorporated in the N-CNTs at all.

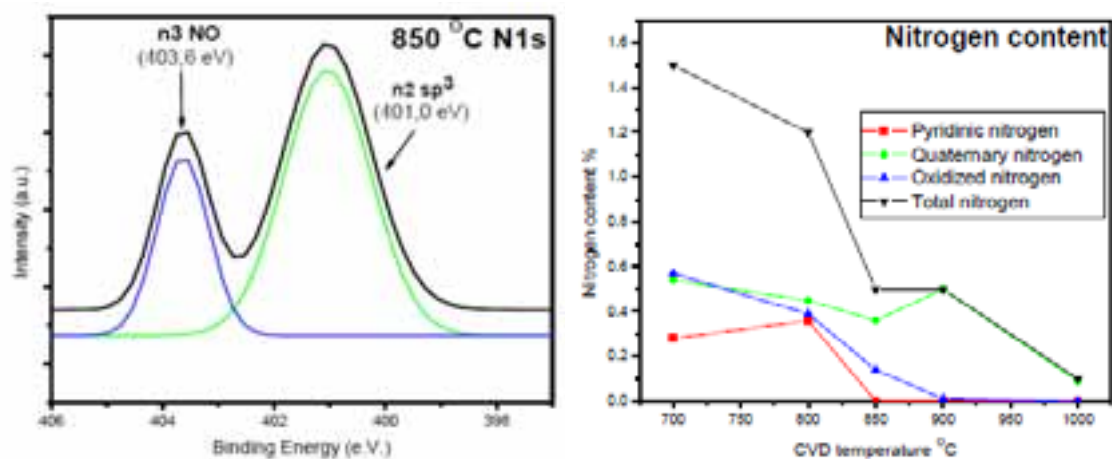


Fig.4: (a) Percentage of types of Nitrogen incorporation in CNT synthesized at different temperatures, extracted from XPS spectra.

Figure 5 shows the four types of nitrogen species that can be incorporated in the graphitic structure of carbon nanotubes. Literature reports that at least four types of nitrogen can be distinguished in the N1s spectrum, viz. pyridinic N (398.6 eV), pyrrolic N (400.5 eV), quaternary- or substitutional N (401.3 eV) and pyridinic N-oxide (402 - 405 eV).

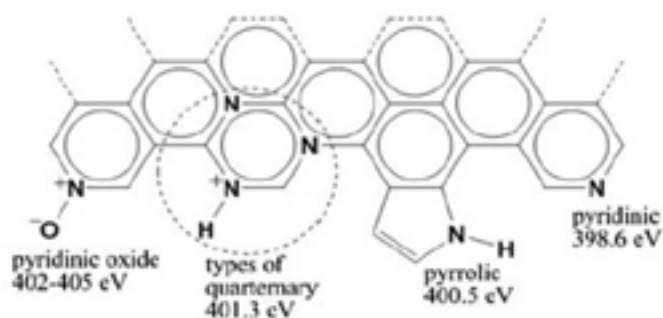


Fig.5: Types of Nitrogen incorporation in graphitic CNTs, and their binding energies (Biddinger *et.al* 2009)

The pyridinic N type is an sp² hybridized nitrogen atom located at the edges or at defects of the graphene sheets. The three sp² hybridized orbitals of pyridinic nitrogen are occupied by four electrons, hence two orbitals are filled by one electron each and form σ bonds with neighbouring carbon atoms while the two remaining electrons form an electron lone pair. The fifth electron is positioned in an atomic p-orbital and is used to form a σ bond with an adjacent carbon atom. The localized electron lone pair has electron donating properties. As with pyridine, the quaternary nitrogen, substituting a carbon atom of the graphitic matrix, has three sp² hybridized orbitals. However, these are filled with one electron each and form three σ bonds with neighbouring carbon atoms. One electron fills an atomic p-orbital and is used to form a π bond with an adjacent carbon atom. The remaining electron cannot be accommodated in a bonding orbital and ends up in a π^* orbital. It is this electron that is delocalized over the graphitic network and is actually delocalized thereby ‘doping’ the graphene layer (Lide 2004, Serp *et al.* 2003, Shimoyama *et al.* 2001).

Nitrogen incorporated in a graphitic environment has both donor properties (because of the extra electron as compared to carbon) and acceptor properties since it is more electronegative than carbon. The delocalized electrons may have an impact on other nitrogen atoms, for example pyridinic types, which may induce changes in their reactivity. Therefore the optimization of the amount of pyridinic nitrogen is important for catalysis. The pyrrolic N type is sp^3 hybridized and part of a five membered ring structure. The quaternary N is a carbon substituted nitrogen atom located in the graphene sheet.

A temperature of 850°C CVD was employed to synthesize CNTs from precursors containing different alcohols. Shorter chain alcohols conduced to more graphitic CNTs that were more thermally stable. It appears from the TGA graph of Fig 6 (a) that butanol gives the optimum stability and purity. Raman spectra (Fig 6(b)) gave higher I_D/I_G peak ratios for shorter alcohols, e.g., ethanol, while I_D/I_G peak ratios were lower for longer chain alcohols. By considering the chain lengths of the alcohols, for the same mass, shorter chain alcohols introduce more oxygen, while longer chain alcohols such as heptanol introduce less oxygen in the precursor. Hence the higher the C:O ratio, the more graphitic the N-CNTs.

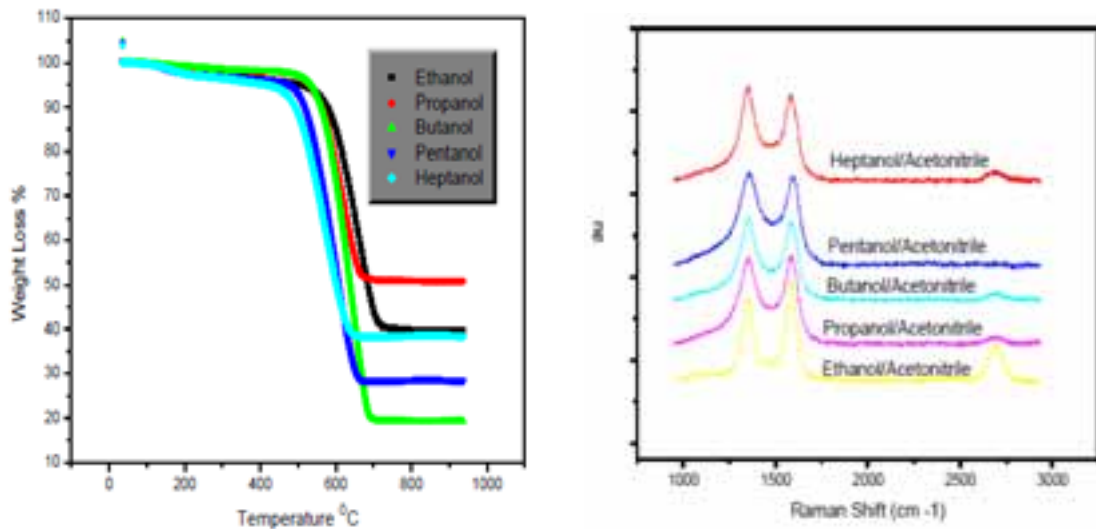


Fig. 6: (a) TGA plots, and (b) Raman spectra, for CNTs synthesized using different alcohols in the precursor at 850°C

We functionalized N-CNTs synthesized at 850 °C from ethanol/acetone nitrile and polymerized P3HT around the CNTs. Figure 7 shows J-V characteristics of ITO/PEDOT:PSS/P3HT:N-CNT/Al solar cells. We observed a slight improvement in the output of the solar cell with polymer attached N-CNTs, as compared to one whose active layer consisted only of P3HT. However the cells with P3HT and N-CNTs that were not functionalized gave much lower outputs.

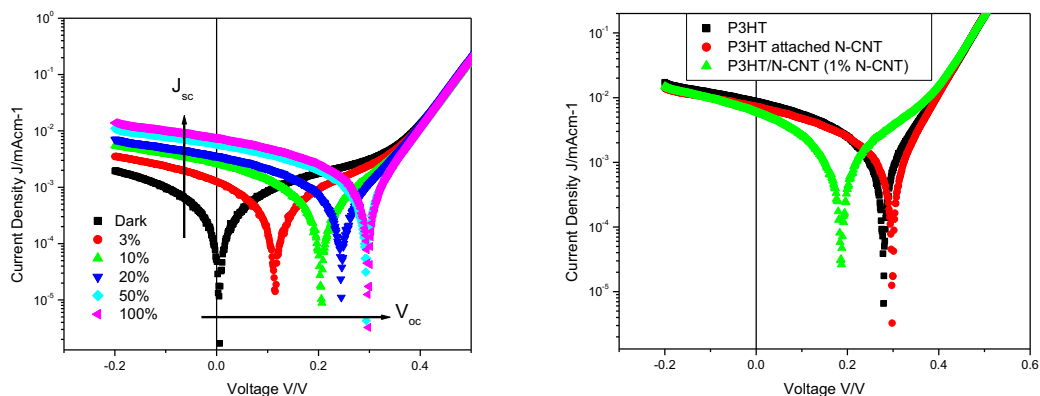


Fig. 7: (a) JV characteristics of a /PEDOT:PSS/P3HT:N-CNT/Al solar cell, (b) Comparison of JV characteristics of solar cells with and without N-CNTs

When the solar cell is illuminated electrons will be excited from the π to π^* states of P3HT, electron transfer from P3HT to the N-CNTs then takes place, producing an excited donor-acceptor radical, and the field at the

interface between P3HT and N-CNTs will dissociate the exciton, hence generating negative and positive charge carriers. The negative charges are transported through the nanotubes to the Al electrode, while the holes are transported by the polymer through the hole transport layer, PEDOT:PSS, which also blocks electron transport, to the ITO electrode. A potential difference is therefore generated between the holes on ITO and the electrons on the Al electrodes, and an electric current is measured in an external circuit. We obtained an open circuit voltage of about 300 mV under white light illumination, and short circuit current densities around 1 mA/cm², with a fill factor FF about 29 %, giving a power conversion efficiency of 0.09 %.

5. Conclusions

A method of controlling the diameters, lengths and graphitic structure of CVD synthesized N-doped CNTs has been demonstrated. Short and thin carbon nanotubes can be useful in carbon based nanoelectronics and photovoltaic devices since there is less entanglement of N-CNTs which will result in good dispersion of carbon nanotubes in solutions and polymer matrix. There is still room for improvement of solar cells incorporating N-CNTs from the materials synthesis as well as from device design and optimization.

6. Acknowledgements

We acknowledge the DST/ Centre of Excellence in Strong Materials of South Africa for funding this research. Dr. R. Erasmus (University of the Witwatersrand) is acknowledged for assistance with Raman spectrometry and Dr. M. Ruemelli (Dresden) for assistance in XPS characterization of some of our samples.

7. References

- Biddinger E. J., von Deak D., Ozkan U. S., 2009. Nitrogen-Containing Carbon Nanostructures as Oxygen-Reduction Catalysts. *Top Catal* (2009) 52:1566–1574.
- Castrucci C., Tombolini F., Scarselli M., Speiser E., Del S.G., Ritcher W., De Crescenzi M., Diociaiutti M., Gatto E., Venanzi M., 2006. Large photocurrent generation in multiwall carbon nanotubes. *Appl. Phys. Lett.*, 89, 253107.
- Chaudhary S., Lu H., Muller A. M., Bardeen, C. J., Ozkan M., (2007). Hierarchical placement and associated optoelectronic impact of carbon nanotubes in polymer-fullerene solar cells. *Nano Letters* 7 (7): 1973–1979.
- Coville N. J., Mhlanga S. D., Nxumalo E. N., and Shaikjee A., 2005. Organometallic precursors for use as catalysts in carbon nanotube synthesis. *Organometal.* 2005, 24. 972–976.
- Lee J. M., Park J. S., Lee S. H., Kim H., Yoo S., and Kim S. O., 2011, Selective Electron- or Hole-Transport Enhancement in Bulk-Heterojunction Organic Solar Cells with N- or B-Doped Carbon Nanotubes, *Adv. Mater.* 23, 629–633.
- Lide D. R., 2004. *Handbook of Chemistry and Physics*, 85th ed., CRC press, Boca Raton, Florida, USA.
- Serp P., Corrias M., Kalck P., 2003. Carbon nanotubes and nanofibers in catalysis. *Appl. Catal. A: Gen.* 253, 337-358.
- Shimoyama I., Wu G., Sekiguchi T., Baba Y., 2001. Study of electronic structure of graphite-like carbon nitride. *J. Electron Spectrosc.*, , 114-116, 841-848.
- Terrones, M., Grobert, N., Terrones, H., 2002. Synthetic routes to Nanoscale B_xC_yN_z architectures. *Carbon* 40, 1665, 1684.
- Terrones, M., Jorio, A., Endo, M., Rao, A.M., Kim, Y.A., Hayashi, T., Terrones, H., Charlier, J.C., Dresselhaus, G., Dresselhaus, M.S., 2004. New Directions of Nanotube Science: Properties, Characterization and Applications of B- and N-doped systems, *Materials Today Magazine* 7, 30-45.