

# Tuning carbon nanotubes for photovoltaic applications

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**Abstract.** Control of diameter and nitrogen doping in the synthesis of nitrogen doped carbon nanotubes (N-CNTs) can be achieved by careful selection of catalyst, precursor mixture and chemical vapour deposition (CVD) synthesis temperature. A solution of methanol and acetonitrile (20% acetonitrile) was pyrolysed over a Fe/Al/MgO catalyst in a CVD reactor at 850 °C. The product was characterised by TEM, TGA and Raman spectroscopy. N-CNTs with well graphitised morphology, small diameter, and narrow diameter distribution were obtained. Catalyst support and metal particles were removed completely during purification without any change in morphology of the material. Organic solar devices were made from P3HT and the N-CNTs synthesized.

## 1. Introduction

Multiwalled carbon nanotubes structurally comprise of several coaxially arranged graphene cylinders of different radii with an inter-tube separation of approximately 0.34 nm. Generally multiwalled carbon nanotubes are synthesized with a range of diameters up to as big as 100 nm [1]. The thickness of the bulk heterojunction organic layer in organic photovoltaic devices is 200 nm. Thus for efficient exciton splitting in the devices the composite film between donor polymer and acceptor material should be nanostructured with less than 20 nm between the acceptor material and the donor material. Because of this, carbon nanotubes of diameters less than 20 nm are most suitable for application in organic photovoltaic devices. During the synthesis of carbon nanotubes for application in organic photovoltaic devices control of diameters then becomes a critical issue. Semiconducting carbon nanotubes are particularly attractive for use in organic photovoltaic devices [2]. It is very difficult to control whether resulting carbon nanotubes are purely metallic or semiconducting as they are both produced as a mixture during synthesis. Separation of semiconducting from metallic carbon nanotubes is a very difficult process. For single walled carbon nanotubes, whether they are metallic or semiconducting depends on their chirality [3]. MWNTs are more complex than SWNTs because it is not only the outer wall which determines the conducting properties of carbon nanotubes. No matter the chirality of the outer wall MWNTs are always metallic in nature [4].

Incorporating heteroatoms in MWNT matrix results in the tuning of the electronic properties of the resulting MWNTs. Doping with boron and nitrogen is the preferred method for changing the

electronic properties of carbon nanotubes. Boron doping yields purely p-type semiconducting carbon nanotubes whilst doping with nitrogen yields purely n-type semiconducting carbon nanotubes [5]. During nitrogen doping incorporating pyridinic nitrogen type in carbon nanotubes is desired. However, in a CVD reaction atmosphere it is not possible to control the type of nitrogen incorporated and hence graphitic, quaternary, oxidized nitrogen and molecular nitrogen are also incorporated within the carbon nanotubes structure.

The diameter of grown MWNTs is influenced by catalyst and temperature used during synthesis [6]. The use of ethanol has been investigated as a co-solvent in the N-CNT synthesis method and it was found that it influences the crystallinity of the produced MWNTs [7]. OH radicals are produced during the reaction and they etch away amorphous carbon material which might be deposited during growth.

## 2. Experimental

To make nitrogen doped carbon nanotubes N-CNTs 300 mg catalyst was placed in a quartz boat inserted in the centre of a quartz tube reactor. The catalyst used in this study was Fe/MgO and Fe/Al/MgO. The reactor was heated to 850 °C in 5% H<sub>2</sub> in Ar flow at 240 ml/min. At 850 °C the carbon and nitrogen source (20% acetonitrile in ethanol) was introduced by means of 20 ml syringe driven by a pump at 1.2 ml/min for 20 minutes. Finally the reactor was cooled to ambient temperature under a flow of 5% H<sub>2</sub> in Ar. The synthesized carbon nanotubes were purified by washing for several hours in dilute NaOH in an ultrasonic bath followed by washing several times with water, refluxing for several hours in hydrochloric acid at 100 °C and lastly by washing in water and drying in an oven at 120 °C for 12 hours. The morphology and quality of the as synthesized N-CNTs was characterized by Transmission Electron Microscopy (Tecnai G<sup>2</sup> Spirit TEM at 120 kV). TGA was also used to characterize the extent of purification of material and the stability of N-CNTs before purification and after purification, using a Perkin Elmer Pyris Thermogravimetric Analyser 1 instrument under air flow.

To fabricate devices, the ITO glass substrate was patterned by etching in acid and cleaned in an ultrasonic bath using detergent followed by several organic solvents and lastly with distilled water. Solutions were prepared by dissolving poly 3-hexythiophene P3HT and the N-CNTs in chlorobenzene and sonicated for ten minutes followed by stirring for twelve hours in a dark inert atmosphere. The device was fabricated by spin coating Poly (3, 4-ethylenedioxythiophene) poly (styrenesulfonate) PEDOT: PSS a hole collecting layer at 2000 rpm followed by the P3HT/N-CNT active material at 2000 rpm and lastly an aluminium top contact was deposited by evaporating in a vacuum evaporator at 10<sup>-5</sup> mbar. Absorption spectra of the P3HT and the P3HT/N-CNT blend were taken using a Varian Cary UV-VIS-NIR spectrometer and I-V characteristics of the devices made were measured in the dark and under illumination (solar simulated radiation with a AM1.5 filter) using an HP 4141 Source Measure Unit.

## 3. Results and discussion

### 3.1. Characterization of N-CNTs

Chemical vapor deposition CVD method for synthesizing carbon nanotubes has the advantage of controlling the properties of as synthesized multi-walled carbon nanotubes. We were able to control the properties of the as synthesized carbon nanotubes used in this study using good catalyst selection, suitable precursor material and growth conditions. The optimum temperature for synthesizing good quality carbon nanotubes with small diameter and low yields (<2%) of amorphous material was obtained at 850 °C. TEM studies revealed that the N-CNTs obtained contained bamboo-like morphologies. When using an iron catalyst the presence of the bamboo morphology confirms the presence of nitrogen incorporation in the carbon nanotubes matrix [8]. The pyridinic like nitrogen is the one responsible for inducing bamboo morphology in nitrogen doped carbon nanotubes [9]. The presence of the pyridinic like nitrogen in nitrogen doped carbon nanotubes introduces electrons in the form of electron lone pair from the pyridinic like nitrogen. This makes nitrogen doped carbon

nanotubes purely n-type semiconducting material [5]. Figures 1 (a) and (b) show a comparison of the multi-walled N-CNTs produced using Fe/MgO and Fe/Al/MgO catalysts respectively. Fig. 1(b) revealed that Fe/Al/MgO produces N-CNTs with smaller and more uniform diameters.

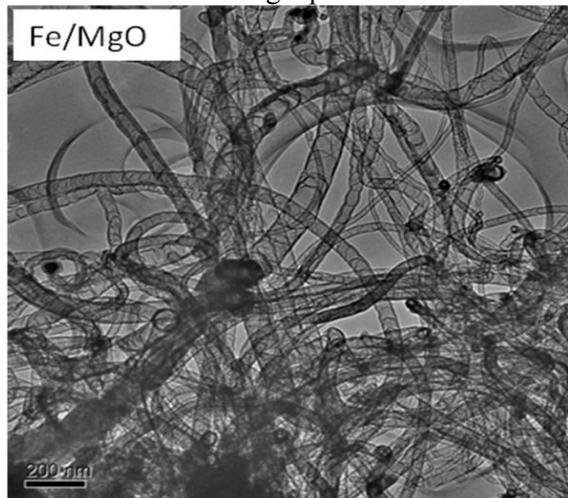


Fig. 1(a) Purified N-CNTs synthesized from Fe/MgO catalyst

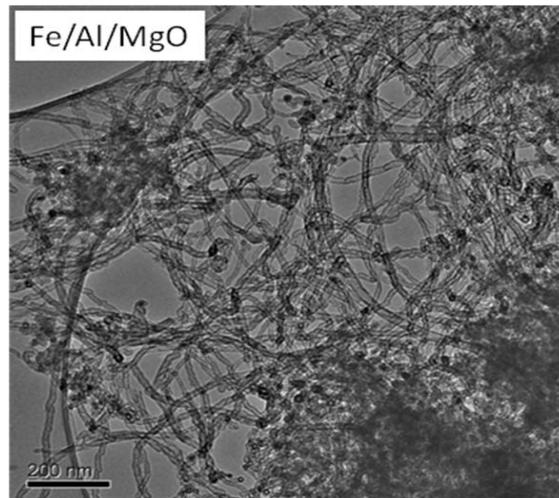


Fig. 1(b) Purified N-CNTs synthesized from Fe/Al/MgO catalyst

From the TEM images in Fig. 1, very little amorphous material is seen, and thermogravimetric analysis (Fig. 2(a)) confirmed this result. The synthesized N-CNTs were thermally stable with a decomposition temperature of 650 °C. After purification using NaOH solution and HCl no additional defects were added on the N-CNT structure as shown by the similarities of the TGA profile of the as synthesized N-CNTs and the purified N-CNTs. Raman spectroscopy (Fig 2(b)) showed an  $I_D/I_G$  of 0.8 for N-CNTs produced from Fe/Al/MgO showing that the N-CNTs have graphitic character.

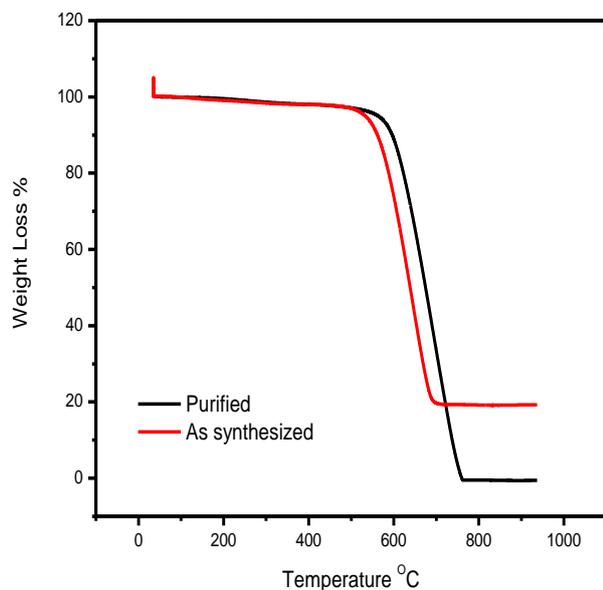


Fig. 2(a) TGA of as synthesized N-CNTs from Fe/Al/MgO catalyst and N-CNTs after purification

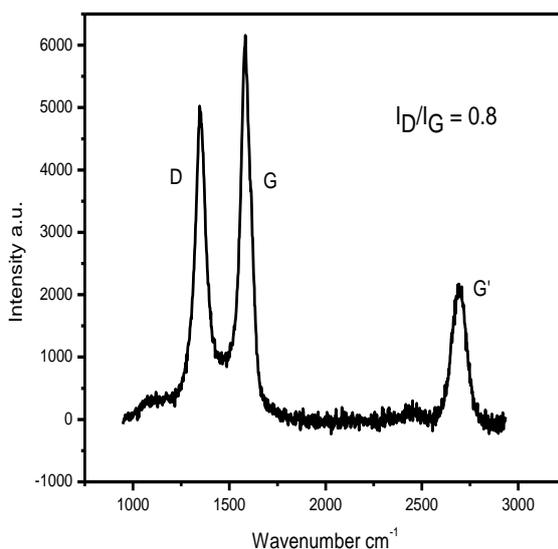


Fig. 2(b) Raman spectra of N-CNTs synthesized from ethanol and acetonitrile mixture at 850 °C over a Fe/Al/MgO catalyst

### 3.2 Solar cells

The thin film photovoltaic devices fabricated were made with the architecture shown in Fig 3 (a), to evaluate the influence of incorporating N-CNTs in P3HT on the device performance.

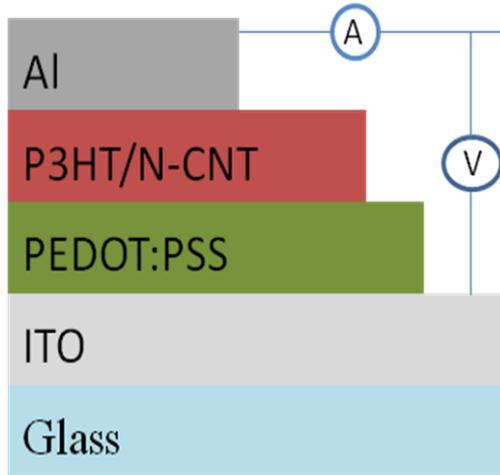


Fig. 3(a) Schematic representation of fabricated P3HT/N-CNT solar cells

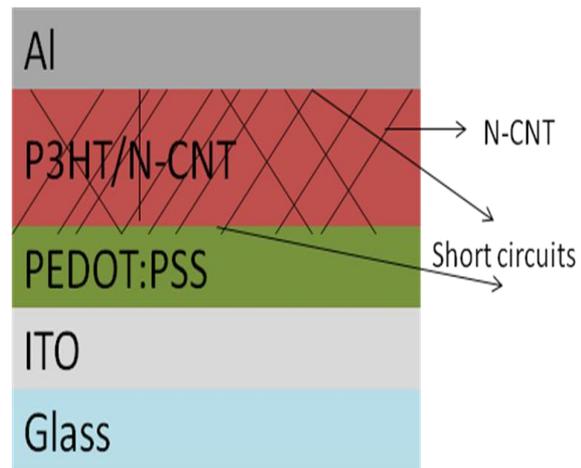


Fig. 3(b) Schematic representation of possible source of poor performance in fabricated solar cells

The 1% N-CNT in P3HT and 5% N-CNT in P3HT showed a decrease in  $I_{SC}$  when N-CNTs were introduced in the active layer but both gave an increase in  $V_{OC}$ . A higher concentration of N-CNTs in the devices (more than 5 %) resulted in decrease of both the  $I_{SC}$  and the  $V_{OC}$ .

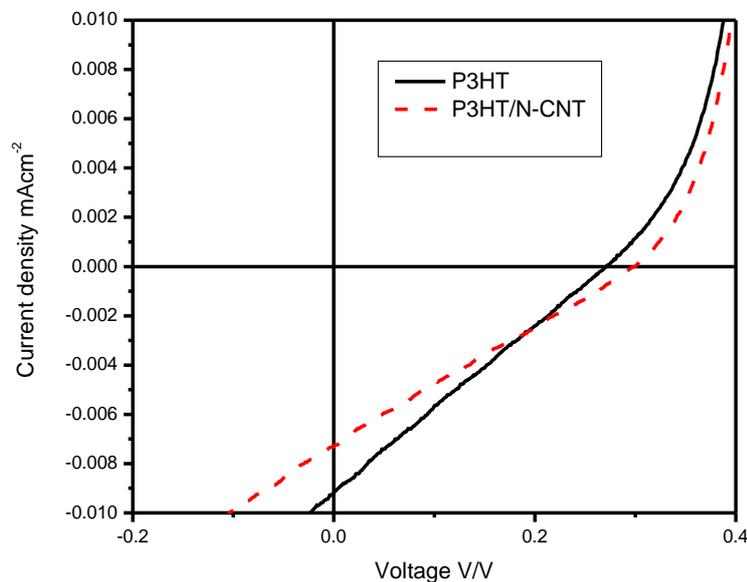


Fig. 4  $J$ - $V$  characteristics of solar cells made from P3HT and P3HT/ 1% N-CNT active materials

The device made from P3HT alone showed an open circuit voltage  $V_{OC}$  of 0.27 V and a short circuit current density  $J_{SC}$  of  $9.1 \mu\text{A}/\text{cm}^2$  and the device made from P3HT/ 1% N-CNT showed  $V_{OC}$  of 0.3 V and  $J_{SC}$  of  $7 \mu\text{A}/\text{cm}$  (see Fig. 4). Incorporating N-CNTs in the P3HT active layer improved charge separation resulting in the small increase in  $V_{OC}$ . An increase in  $V_{OC}$  results from efficient exciton splitting and charge separation. In this work we synthesized N-CNTs which are said to be purely n-

type semiconducting [5]. Interaction between the n-type N-CNTs and the p-type P3HT resulted in good electron hole pair dissociation. The  $I_{SC}$  does not behave the same way as the  $V_{OC}$ . A decrease in  $I_{SC}$  after incorporation of N-CNTs was noted. The N-CNTs used in this study were very long, generally more than  $1\mu\text{m}$  long (Fig.1 (b)). We suspect that this resulted in them spanning both electrodes and shorting the devices as shown in Fig 3(b). The photogenerated charge carriers in the N-CNTs travel to both the anode and cathode thus diminishing the photogenerated current as it is possible that the current will be flowing in opposing directions.

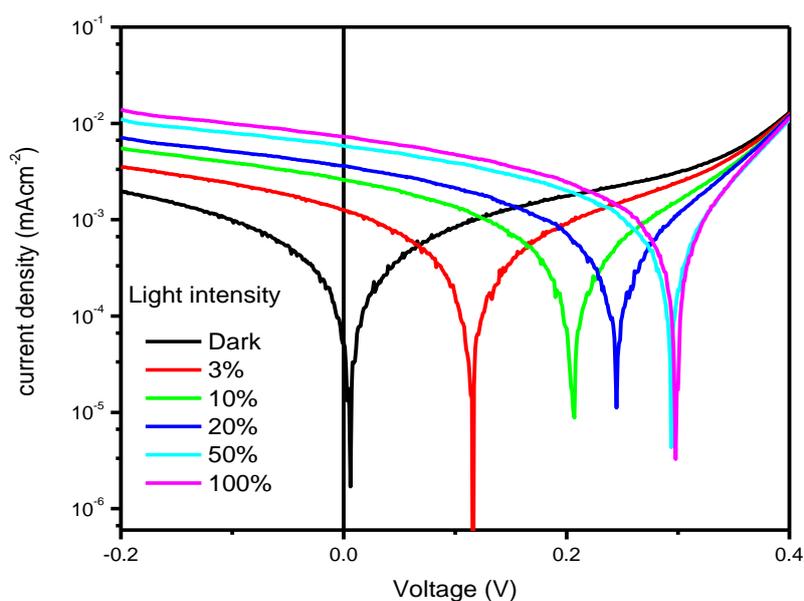


Fig. 5 Semi log plot of  $J$ - $V$  characteristics of solar cells made from P3HT/1% N-CNT at different light intensities

Under AM 1.5 spectral illumination with light of different intensities the P3HT/N-CNT showed a photo-response as shown in Fig 5.

#### 4. Conclusions

The ability to control the diameter of N-CNTs using catalyst selection and carbon and nitrogen source has been demonstrated. The use of the synthesized materials in the fabrication of solar cells yielded P3HT/N-CNT solar cells with enhanced  $V_{OC}$  but diminished  $I_{SC}$  as compared to the devices made out of P3HT alone. Optimization of concentration of N-CNTs in P3HT matrix is needed to obtain solar cells with improved performance. Improved device fabrication methods and application of short N-CNTs in organic photovoltaic devices is expected to enhance performance. Shortening of N-CNTs will be done during synthesis by keeping short reaction times or after synthesis by ultrasonication for long hours.

#### Acknowledgements

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