

Synthesis and characterization of nitrogen-doped CNTs and carbon-coated GaN nanostructures: sensor and solar cell applications

by

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Declaration

I declare that this is my own, unaided work, other than where acknowledged. It is being submitted in fulfilment of the requirements for the degree of Doctor of Philosophy in Physics to the University of the Witwatersrand, Johannesburg. It has not been submitted for any degree or examination in any other university.

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Abstract

Carbon based nanostructures have inspired extensive research due to their superior physico-chemical and electronic properties which can be tuned through doping with heteroatoms on the surface or at the ends. Besides their high surface to volume ratio and thermal stability have seen them being explored as promising candidates for sensor applications either as active layer or as templates for active layer support. In addition the ballistic transport of the charge carriers opens up applications as transparent conducting electrodes in photovoltaic technology and fast response electronic devices. The aim of this work was to design nitrogen doped carbon nanostructures based sensors for diverse applications in standard and harsh environments. The synthesis and functionalization of nitrogen doped carbon nanotubes (aligned and non-aligned) either as carbon coated GaN or metal oxide or chalcogenide based carbon nanostructures allow for application in sensors and hybrid photovoltaic devices to monitor harmful gases in the environment as well as to reduce or eliminate global warming.

Chemical vapour deposition (CVD) was used to fabricate nitrogen doped carbon nanotubes (N-CNTs) and aligned N-CNTs (A-N-CNTs). The N-CNTs acted as a support for the transition metal-VI alloys (SnO_2 and CdS) based nanomaterial encapsulated on the nanotube surface. The optimized N-CNTs coated with SnO_2 were tested for detection of H_2 , CO , NH_3 and CH_4 gases at room temperature and 250°C . The sensor showed no response to all the gases at room temperature. However the response to NH_3 , CO and H_2 was observed at 250°C . The sensitivity to NH_3 at 250°C surpassed its sensitivity to any other gas studied in the temperature range investigated.

The A-N-CNTs were synthesised using an aerosol assisted CVD with a fixed concentration of ferrocene catalyst. The magnetic properties of the residual impurities in the A-N-CNTs made up of Fe-nanoparticles (NPs) left after the purification process were investigated using hyperfine interaction techniques and a SQUID magnetometer. Mössbauer spectroscopy studies revealed the presence of $\alpha\text{-Fe}$, $\gamma\text{-Fe}$, Fe_2O_3 and Fe_3C . This was further confirmed by the magnetization curves with high coercive fields indicating the presence of size effects on the magnetization and coercivity. Nitrogen doping was used to limit the concentration, shape and aspect ratio of NPs embedded in the cavity of the carbon nanotubes through the formation of bamboo like structures.

As a proof of concept GaN and carbon coated GaN (C-GaN) have been implemented as active layers in sensors for detection of CO, NH₃, CH₄ and H₂ gases at room temperature and 250 °C. The sensor based on pure GaN have shown no response to all gases at these temperature ranges. However, C-GaN sensors response to all the four gases was observed and the mechanism of function identified to be driven by surface defects sites on the carbon coated GaN. The sensor (C-GaN TA) responded better compared to C-GaN CN (C-GaN TA (carbon source toluene (T) and Ar as carrier gas) and C-GaN TN (carbon source acetylene (C) and N₂ as carrier gas). The ability for C-GaN to respond to CO, NH₃, CH₄ and H₂ gases at room temperature opens up the possibility for its easy use in indoor and outdoor monitoring.

Dedication

This work is dedicated with love to my late parents.

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ABBREVIATIONS

1D	One dimension
AACVD	Aerosol assisted chemical vapour deposition
A-CNT	Aligned carbon nanotubes
Au	Gold
BET	Brunauer Emmett Teller
BHJ	Bulk heterojunction
CCD	Charge coupled device
CdS	Cadmium sulphide
CH₃CN	Acetonitrile
CH₄	Methane
C-GaN	Carbon coated Gallium nitride
CNTs	Carbon nanotubes
CO	Carbon monoxide
CuO	Copper (II) oxide
CVD	Chemical vapour deposition
CdS	Cadmium sulphide
D	Doublet
DC	Direct current
ESR	Electron spin resonance
FET	Field effect transistors
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width half maxima
GaAs	Gallium Arsenide
GaN	Gallium nitride
H₂	Hydrogen
H₂S	Hydrogen sulphide
HEMTs	High electron mobility transistors
HNO₃	Nitric acid
HOMO	Highest occupied molecular orbital
IPVCs	Inorganic photovoltaic solar cells
ITO	Indium tin oxide

J_{max}	Current density at maximum power
J_{sc}	Short circuit current density
J-V	Current density
LUMO	Lowest unoccupied molecular orbital
MWCNTs	Multi-wall carbon nanotubes
N-CNT	Nitrogen-doped carbon nanotubes
NH₃	Ammonia
NO₂	Nitrogen dioxide
NPs	Nanoparticles
OPV	Organic photovoltaic device
OPVCs	Organic photovoltaic solar cells
OSC	Organic solar cells
P3HT	Poly(3-hexyl-thiophene-2,5-diyl)
PCE	Power conversion efficiency
PCBM	phenyl-C61-butyric acid methyl ester
Pd	Palladium
PEDOT:PSS	Poly(3,4-ethylenedioxylenethiophene):poly(styrenesulfonic acid)
PL	Photoluminescence spectroscopy
P_{max}	Maximum power
Pt	Platinum
PXRD	Powder X-ray diffraction
QS	Quadrupole splitting/shift
R_s	Series resistance
R_{sh}	Shunt resistance
SCCM	Standard cubic centimetres per minute
SEM	Scanning electron microscopy
S	Single line
SnO₂	Tin dioxide
SQUID	superconducting quantum interference device
SWCNTs	Single wall carbon nanotubes
SX	Sextet
TEM	Transmission electron microscopy
TGA	Thermal gravimetric analysis
V_{max}	Voltage at maximum power

Voc	Open circuit voltage
WO₂	Tungsten (IV) oxide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Chapter 1: Introduction

1.1 General overview

Human activities have been characterized by a rise in the demand for energy and the search for novel alternative energy sources to improve energy efficiency. As a consequence, the energy sources have led to deleterious effects on the environment. These effects are associated with the emission of toxic or greenhouse related gases that have unprecedented climate change that adversely impact humanity. These two mutually exclusive challenges thus call for the development of highly efficient devices to sense emitted gases and for efficient energy conversion. To this end, efforts have been expended to develop new materials with high performance benchmarks for sensor and photovoltaic applications. Among the materials choices that have been considered are the one-dimensional low Z nanostructures such as carbon nanotubes and they have shown great promise for the development of chemical sensors [1], [2], [3], [4], [5], biological (CNTs) sensors [6], [7] and solar cells [8]. Besides, carbon nanostructures have been developed with varied quantum confinement effects, superior opto-electronic and thermal properties.

On the energy front, renewable energy has been driven by the need for an environmentally friendly and sustainable resources. Currently, solar energy is viewed as a viable option due to the decreasing costs on the production of solar cells. In addition the energy derived from solar cells is abundant, clean and renewable unlike their fossil fuels counterparts which are harmful to the environment and have a finite lifetime.

The excellent property of CNTs which allow tenability that is specific to particular applications has seen these materials being intensively investigated for a suite of applications. Besides, these materials allow for greater functionality with other materials leading to improved performance due to their enhanced optoelectronic and electrochemical properties. CNTs also offer significant opportunities to improve solar cell efficiencies by facilitating photon absorption, electron transport and collection [9]. Carbon nanotubes (CNTs) are also used in solar cell applications because of their high-work function [10]. CNTs have been introduced into conjugated polymers to produce organic photovoltaic devices [11]. CNT-based heterojunctions are of particular interest in organic photovoltaic cells because of their unique geometry as well as their excellent electronic, thermal and mechanical properties [12]. Organic solar cells are flexible and their production costs are only about a third of the price of a silicon cell. They can be designed on a molecular level [9]. The combination of lower cost and better adaptability makes organic photovoltaic cells very appealing.

Doping entails the intentional introduction of foreign atoms ('heteroatoms') into the CNT lattice. The study of doping of CNTs with heteroatoms has recently attracted considerable interest, since doping is known to induce superior electronic properties into the nanomaterials and provide a means of tuning the field emission of CNT emitters [13], [14], [15], [16]. It has been shown theoretically and experimentally that nitrogen and boron doping significantly enhance the mechanical, conducting, magnetic, field emission, energy storage and electron transport properties as well as the catalytic activity of CNTs [17], [18], [19], [20], [21], [22], [23]. Interestingly, a doped CNT material leads to enhanced electronic performance with thermal conductivity of between 2000 – 6000 W/mK at 25 °C [24] due to the participation of an additional lone pair of electrons in the delocalised system of the hexagonal framework. Nowadays, the study of CNT doping has entered an explosion growth regime due to the potential use of doped CNTs as field effect transistors, logic circuits, sensors, in gas storage and adsorption, and as fillings of reinforced composites, *etc.* [25], [26], [27]. Nitrogen behaves as an electron donor when doped into the graphitic structure and this enhances the CNT conductivity. Thus, the chemical structure of the nitrogen doped CNT (N-CNT) is expected to be strongly dependent on its synthesis route. Many researchers have demonstrated that the morphology and chemical composition of N-CNTs and N-CNT growth depends largely on the experimental procedures used [28], [29], [30], [18].

1.2 Motivation of the study

The functionality of sensor materials are based on the rapid response, recovery and high sensitivity within a defined range of temperatures and gaseous ambient. These properties can be effectively tuned by changing the surface to volume ratio without compromising the signature of the response to minute quantities of analyte or gas. The recyclability of the response and recovery is greatly determined by the nature of the surface electronic properties and their characteristics under diverse gaseous environment or adsorption. Of the materials that have shown promise include carbon nanostructures that have been functionalized through doping or decoration with sensor active bulk materials to provide for enhanced active sites on the CNT anchors. SnO₂, CdS and GaN have been applied in the bulk as gas sensors. CNT-SnO₂ exhibited enhanced gas sensing properties involving reduction of the resistance of the sensors or improvement of gas sensitivities, and may possibly be potential novel materials for gas sensors [19]. However, their sensitivities were still very low. CNTs exhibit a low chemical reactivity with the gas molecular environment due to their strong sp² bonding and near perfect hexagonal structure [20]. Multiwall carbon nanotubes (MWNTs) are not very sensitive to ambient gas [21]. To overcome these drawbacks and to extend the application

of CNTs in gas sensing field by achieving faster response, good reversibility and selectivity, CNT side walls are modified with functional materials, such as metal oxides, polymer, noble metals like palladium, platinum, gold [22], [23] likewise semiconductor cadmium sulphide (CdS), an important functional material has been studied in recent years to examine its decoration on CNT [31], [32]. The present work focuses mainly on the doping of N-CNTs and the loading of transition metals based compounds on N-CNTs. These binary metal compounds constitute cadmium sulphide (CdS) on N-CNTs to increase its efficiency in a solar cell and tin oxide (SnO₂) and CuO for enhancement of sensitivity in gas sensor studies.

Besides the use of the materials anchored on the CNT backbone, the control of the size of the ferromagnetic catalysts can be exploited for their tuneable magnetic fields. Magnetic sensors can thus be achieved by intentional dopant incorporation of ferromagnetic atoms. However, control of the impurities that remain embedded within the tubes pose a major challenge for the application of CNTs in magnetic, electronic, or/and related devices [33]. To solve some of the problems associated with the metal nanoparticles, recent research reports have indicated that the structural orientation (vertically aligned or randomly) of CNTs can be an interesting area of study. For instance, aligned CNTs (A-CNT) are useful as sensors due to their large surface area [34]. Thus evaluating the magnetic properties of the N-doped vertically aligned MWCNTs containing residual impurities could be the keynote to finger print the purification process and as well as understand the role of nitrogen doping.

CNTs synthesized by CVD usually contain other unwanted materials like metal particles, amorphous carbon and fullerenes. Hence an effective mechanism for purification of the CNTs is required before further use [35]. Most of the existing gas sensors used commercially are solid state materials (e.g. SiO₂, GaAs, SnO₂, WO₂ etc). In this study chemical strategies will be used to make N-doped CNTs and carbon doped GaN nanostructures. GaN is a wide-band gap (3.39 eV at room temperature) semiconductor with excellent thermal stability [36]. GaN has a high potential for applications in optoelectronic and electronic devices such as light emitting diodes (LEDs) [37], laser diodes [38], zero-dimension quantum dots [39], two-dimension quantum wells [40], field emission transistors, integrated circuits etc. The demand for reliable and fast gas detection devices with high sensitivity has led to the choice of using N-doped CNTs as well as carbon doped GaN nanostructures in this study. In this study chemical strategies will be used to make N-doped CNTs and carbon doped GaN nanostructures. The synthesis and characterization of nitrogen doped CNTs, aligned N-CNTs and GaN and their properties under various conditions will be carried out.

CNTs are synthesized by three different methods namely: electric arc-discharge [41], laser ablation [42] and CVD [43]. Among these techniques, the CVD process is generally the most widely used technique because it is cost effective, commercially viable and gives materials of high purity. The supported catalyst [44] and the floating catalyst [45], [46], [47], [48], [49], [50] methods are the most common of the CVD techniques used in most studies.

The demand for reliable and fast gas detection devices with high sensitivity has led to choosing N-CNTs as well as carbon doped GaN nanostructures as materials of interest in this study

Most of the efficient solar cells materials in the market are based on silicon as the photoactive layer. However the cost per energy in the fabrication of silicon is prohibitive thus leading to the search for alternative low cost energy materials to replace it. CNTs have been shown theoretically to be a potential replacement for silicon. The doping of CNTs with nitrogen produces defects and thus modifies both the chemistry and the electronic properties of the CNTs. This approach is a powerful strategy to fabricate N-doped CNTs. For the growth of aligned N-doped CNTs the pyrolysis of ferrocene (FeCp₂) and acetonitrile (ACN) will be used [51]. Nitrogen behaves as an electron donor when doped into the graphitic structure and this enhances the CNT conductivity [52], [53], [54], [55]. Thus, the chemical structure of N doped CNTs (N-CNTs) is expected to be strongly dependent on its synthesis route. Many researchers have demonstrated that the morphology and chemical composition of N-CNTs and N-CNT growth depends largely on the experimental procedures used [56], [57], [58], [17]. However, it has so far been shown that the efficiencies of N-CNTs in organic photovoltaics solar cells are still very low. Low carrier mobility of organic materials is one of the factors contributing to low efficiency in organic solar cells (OSCs).

1.3 Aims and objectives of the research project

The drive for fast response, high active site density and recovery in low dimensional carbon nanostructures has been exploited for sensor applications. The response of the active layer can thus be tuned by changing the surface-volume relationships through chemical modification of the nanomaterial structure or surface through doping or surface decoration. N-CNTs have been studied for sensor and solar cell applications and these nitrogen doped aligned carbon nanotubes provide high surface area and active sites that act as a matrix or template for sensor and solar cell applications. Additionally, the high thermal stability of these materials enables them to be operated

at elevated temperatures. Besides the electrochemical characteristics of the surface, carbon nanomaterials have found applications in energy storage and conversion. To expand on these studies, we have decorated the N-CNTs and GaN with different materials GIVE THEM as the addition to the photoactive surface could enhance the sensor and solar cell properties (photo-absorption and fast charge transfer) of the underlying N-CNTs and GaN.

1.3.1 Synthesis of functional carbon nanomaterials;

The aim will be achieved through the following objectives:

Synthesis and optimization of materials using CVD and aerosol assisted CVD (AACVD) procedures. The materials include;

- (a) N-doped CNTs (N-CNTs) and the use of N-CNTs as a template to load metal oxides and sulphides
- (b) Vertically aligned N-doped CNTs (A-CNTx) and
- (c) Carbon coated GaN nanostructures (C-GaN).

1.3.2 Property optimization in functional carbon nanomaterials;

In this objective the characterization of the properties of the synthesized materials will be iteratively carried out to establish the optimal properties requisite for sensor and photovoltaic applications. In this regard the following techniques have been selected to elucidate the specific properties of the materials and their application potential.

Powder X-ray diffraction (PXRD), Raman spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), photoluminescence (PL) spectroscopy, Mössbauer spectroscopy, the magnetic properties using DC SQUID (Superconducting Quantum Interference Device), electron spin resonance (ESR) spectroscopy and X-ray photoelectron spectroscopy (XPS).

1.3.3 Applications of nanostructured materials in sensors and solar cell devices

The optimized nanomaterials will be investigated as a proof of concept through incorporation into sensor and solar cell devices. The necessary and sufficient performance benchmarks specific to each application were studied.

1.4 Structure of the thesis

This thesis is divided into 8 chapters. A brief explanation of the aims of each chapter is given below:

Chapter 1: This chapter gives the motivation, aim and objectives of the study. A general outlook of the work is further presented in this chapter.

Chapter 2: This chapter presents a brief background on N-CNTs, N-CNTs loaded metal oxides and sulphide, A-N-CNT and C-GaN for diverse applications: It presents a general review on the properties, fabrication and applications of carbon nanomaterials with specific focus on pristine and doped CNTs. The chapter gives a general overview of the mechanism of production, conductivity and electrical properties of carbon nanotubes as well as its use in various applications. Introduction to CNT modification (including surface functionalization and doping) is also reported. The emphasis on this review was placed on work carried out in South Africa. On the application, a review on the sensor and photovoltaic based devices is presented as well.

Chapter 3: This chapter explores the methods used in the production of the nanomaterials as well as the techniques that have been used to evaluate the properties of these materials.

Chapter 4: This chapter presents a report on the “Loading of metal oxides and sulphide on nitrogen-doped multi-walled carbon nanotubes (N-CNT)”. In this chapter, we explore the properties of N-CNTs synthesised by CVD. The study will also look into the application of the prepared materials for sensor and solar cells applications.

Chapter 5: This chapter present an extensive study of “Synthesis and characterisation of aligned nitrogen-doped multi-walled carbon nanotubes (A-CNT_x)”. This work has been published online: I.B. Usman et al., *Materials Chemistry and Physics*; 209 (2018) 280 – 290.

Chapter 6: This chapter reports on the “Properties of carbon coated GaN nanostructures for sensor application”.

Chapter 7: This chapter explores application of the novel materials in sensor and solar cell devices. Detection of greenhouse gases such as CH₄ and H₂ as well as toxic gases such as CO and NH₃ are reported and discussed in detail in this chapter.

Chapter 8: This chapter gives the general conclusions and future outlooks that emanated from the study.

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Chapter 2: Literature Review

2.1 Introduction

A carbon nanotube (CNT) is a high aspect ratio (diameter nm; length μm) tubular structure consisting of carbon atoms in diverse bonding configurations [1], [2], [3], [4]. Interest in these materials was inspired by the report due to Ijima in 1993 [5] on their exceptional mechanical [6], electronic [7] and thermal [8] properties. Depending on the configuration of the carbon atom and on the number of layers within the tubular structure, two types of carbon nanotubes have been identified, namely; the single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs consist of a single graphene sheet seamlessly wrapped into a cylindrical tube (Figure 2.1). MWCNTs on the other hand comprise of an array of such nanotubes that are concentrically nested like rings of a tree trunk [9]. The structure of the nanotubes determines the majority of their properties. Their symmetry is related to the orientation of the hexagonal lattice with respect to the axis of the tube (chirality). Depending on the chirality, a carbon nanotube shows either metallic or semiconductor behaviour [10]. Thus, this allotrope of carbon exhibits morphological, physical and chemical properties: a high aspect ratio (a length-to-diameter ratio greater than 10 000 and as high as 132 000 000) [11], an extremely high conductance [12], a high structural flexibility [13] and thermal conductance [14]. With a high tensile strength [15] and elastic modulus [16], CNTs form the strongest and stiffest synthetic material ever created. The unique combination of properties offer a wide range of potential applications [9], [17], in electronic devices, energy storage and transport, as functional nanocomposites and as drug delivery devices.

Despite the structural similarity to a single sheet of graphene, SWCNTs may be either metallic or semiconducting, depending on the sheet direction about which the graphene sheet is rolled to form a nanotube cylinder. Theoretical studies of the electronic properties of SWCNTs, suggest that nanotube shells can be either metallic or semiconducting, depending critically on the helicity (Fig. 2.1) [18]. The direction in the graphite sheet plane and the nanotube diameter are obtainable from a pair of integers (n, m) that denote the nanotube type [19]. Depending on the appearance of a belt of carbon bonds around the nanotube diameter, the nanotube is either of the armchair ($n = m$), zigzag ($n = 0$ or $m = 0$), or chiral (any other n and m) variety. All armchair SWCNTs are metals; those with $n - m = 3k$, where k is a nonzero integer, are semiconductors with a tiny band gap; and all others are semiconductors with a band gap that scales inversely with the diameter of the

nanotube [19]. The electronic properties of perfect (defect free) MWCNTs are rather similar to those of perfect SWCNTs, because of the weak van der Waal coupling between the cylinders MWCNTs. The nearly one-dimensional structure enables the electronic transport in metallic SWCNTs and MWCNTs to be of ballistic nature (i.e., without scattering) over long nanotube lengths. Thus electrons can carry high currents with essentially no heating or scattering [20], [21]. Phonons also propagate easily along the nanotube with a mean free path of between 500 and 700 nm at room temperature [22], [23]. The measured room temperature thermal conductivity for an individual MWCNTs (3000 W/m.K) is greater than that of natural diamond and that of the basal plane in graphite (both 2000 W/mK) [24]. Superconductivity has also been observed, but only at low temperatures, with transition temperatures of 0.55 K for 1.4-nm-diameter SWCNTs [25] and 5 K for 0.5-nm-diameter SWCNTs grown in zeolites [26]. The synthesis of CNT by CVD methods is performed in the presence of metal catalyst (Fe, Co, Ni) with limited solubility in carbon can thus remain embedded in the tubular structure. Complete purification of the “as prepared” CNTs by nitric acid is difficult as there is always some traces of metal residue thus creating magnetic nanoparticles [27]. The purification process does not completely remove the metal contamination from CNTs. CNTs are diamagnetic in nature and by introducing defects in them they exhibit paramagnetic behaviour [28] as a result of the metal residue encapsulated within the nanotubes.

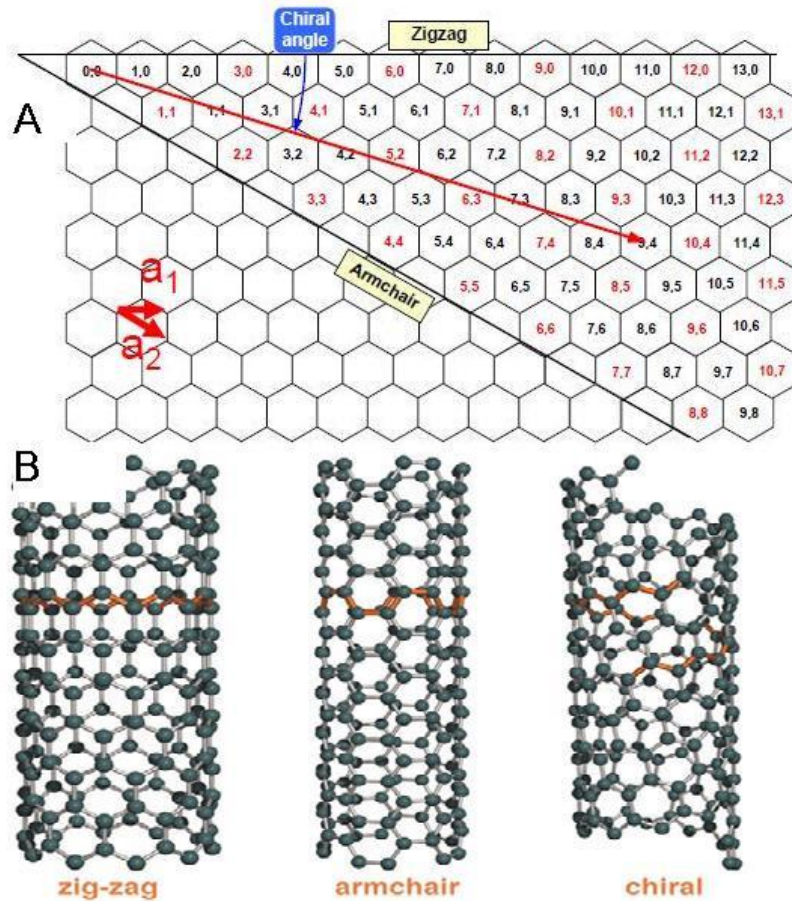


Figure 2-1: A sheet of graphene rolled to show formation of different types of single walled carbon nanotube [29].

2.2 Nanotubes synthesis and processing

CNTs (SWCNTs and MWCNTs) are prepared by carbon-arc discharge [30], laser ablation of carbon [31], [32] or chemical vapour deposition (typically on catalytic particles) [33]. Most of these processes take place in vacuum or in a chamber backfilled with process gases. High quality and large quantities of nanotubes can be synthesized by these methods [34], [35]. In the CVD process a mixture of hydrocarbon, metal catalyst along with inert gas is introduced into the reaction chamber (Figure 4a). During the reaction, nanotubes form on the substrate by the decomposition of hydrocarbons at temperatures of between 700 – 900 °C and atmospheric pressure [36], [37], [38]. The diameter of nanotubes that are to be grown are related to the size of the metal particles. Nanotube diameters range from 0.4 to 3 nm for SWCNTs and from 1.4 to at least 100 nm for MWCNTs [39]. In this process, thermal decomposition of a hydrocarbon vapour is achieved in the presence of a metal catalyst (Figure 2.2). Hence, it is also known as thermal CVD or catalytic

CVD (to distinguish it from many other kinds of CVD used for a variety of purposes). CVD is widely used because of its low cost, high production yield, and ease of scale-up [40].

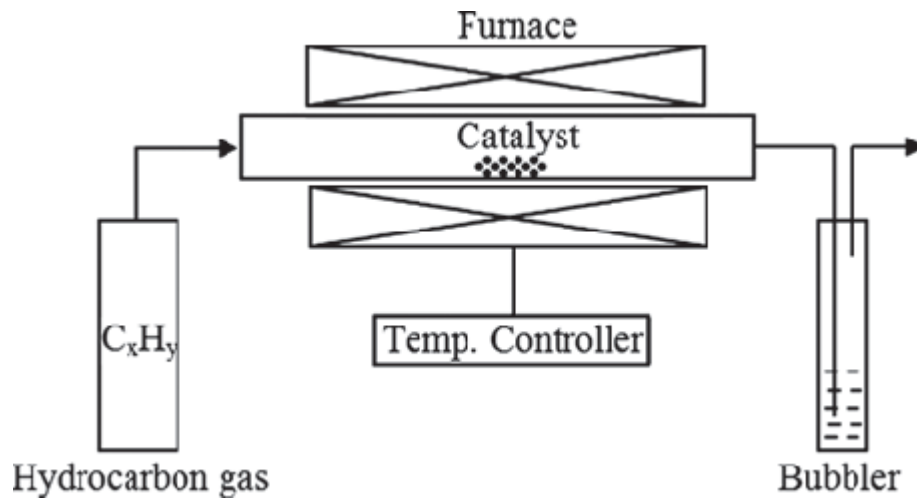


Figure 2-2: Schematic diagram of a CVD set-up [41].

2.3 Applications of CNTs

Since their discovery, carbon nanotubes (CNTs) have generated great interest due to their exceptional properties related to their one-dimensional character [42] like a high current-carrying capacity, high thermal conductivity and reduced charge carrier scattering. The use of both individual nanotubes and CNT networks has been explored, depending on the specific applications [43]. Currently they are used in various technological applications, such as microelectronics or nanoelectronics, the automotive field, telecommunications, the aerospace industry, and the biomedical field. As one-dimensional nanostructures e.g nanotubes of carbon, these materials are being exploited for development of chemical sensors [44], [45], [46], biological sensors [47], [48] and solar cells [49], [50], [51], [52]. They offer significant opportunities to improve efficiencies of solar cells by facilitating photo-absorption, electron transport and collection [53]. Carbon nanotubes (CNTs) are also used in solar cell applications because of their high-work function [54]. CNTs have been introduced into conjugated polymers to produce organic photovoltaic devices [55]. CNT-based heterojunctions are of particular interest in organic photovoltaic cells because of their unique geometry as well as their excellent electronic, thermal and mechanical properties [56].

Organic solar cells are flexible and their production costs are only about a third of the price of silicon based solar cell device. They can be designed on a molecular level [57] and, they are also disposable. The combination of lower cost and better adaptability makes their application in organic photovoltaic cells very appealing. Energy derived from solar cells is abundant, clean and renewable. Solar cells are environmentally friendly, unlike fossil fuels which are harmful to the environment. The properties of CNTs can be tuned to particular applications and in some cases incorporated with other materials to improve the performance of the electronic device.

Several sensors have been utilized for analyte detection in environmental monitoring, medical diagnostics, food safety and security. These devices have been predominantly developed using CNTs [58], [59] as the electro-active surface or template. The increased application of CNTs in chemical sensors is largely driven by their large surface area which provides active sites for molecular gas adsorption [44], [60], [61] as well as superior gas absorption and release capabilities. These properties are ideal for environmental applications [62]. The sensing mechanism of CNT-based gas sensors is mainly associated with p-type semiconductivity [63]. Generally, the electrical conductance of CNTs is modified through the electron transfer between the CNTs and the oxidizing or reducing gas molecules adsorbed on the CNT's surface. Hence the electrical resistance of p-type CNTs decreases when the concentration of the adsorbed oxidizing gas molecules increases [64]. These characteristics make them attractive for gas sensors applications.

The high surface-to-volume ratio, high electron mobility, great surface reactivity and high capability of gas adsorption, CNTs can be used as sensitive layers in gas sensors for environmental monitoring, industrial process control and non-invasive biomedical analysis, by exploiting the changes in their electrical characteristics induced by surface chemical modifications [65]. Defects in CNTs play a crucial role in the electronic, optical and mechanical properties [66]. Defects such as pentagons, heptagons, vacancies, or dopant are found to modify drastically the electronic properties of these nanosystems [67]. The defects can be preferred depending on the nature of the application: for example, for sensor applications, nanotubes with structural defects are more desirable than ideal CNTs [68], [69], as they provide for a strong interaction between the adsorbing species and the defective sites. The ability to tune the occurrence of the defects and their concentration in CNTs provides for greater control of the sensing mechanism and characteristics. Furthermore, depending on the kind of defects, the binding energy can be tuned and recovery mechanisms after gas molecules have been adsorbed on the CNT wall defects modified to yield the optimum response.

2.4 Incorporation of nitrogen

The incorporation of nitrogen into CNTs significantly influences the structure of the pristine carbon nanostructure. Indeed the location of the dopant site such as on the walls of MWCNTs provides an attractive approach for tuning their chemical and electrical properties [70], [71], [72]. Nitrogen doped CNTs exhibit better performance as electron emitters [73], [74], [75]. Electrochemical reactivity and porosity of the tubes is enhanced via N incorporation because pure CNTs are chemically inert. Hence, functionalization or surface modification is required to make them chemically active. In this context, doped tubes have superficial defects that decrease the chemical inertness of pure CNTs. It is worth mentioning that N-doped MWNTs take advantage of defective sites as a mechanism for wall functionalization [76], [77] and reaching high doping levels is the ultimate goal. Furthermore, this particularly high wall reactivity of N-containing CNTs makes them ideal components in fast gas sensors as previously demonstrated in the work of Villalpando-Paez *et al* [78]. N-doped MWCNTs have been used as matrix fillers in composite materials due to their improved electrical conductivity which is generated by the N incorporation. The improved electronic properties are coupled to superior mechanical properties. The additional lone pairs of electrons due to nitrogen contribute electron carriers to the conduction band [79], thus rendering nitrogen-doped carbon nanotubes (N-CNT) either metallic or degenerate semiconductors [80]. Hence, nitrogen doping has been considered as a feasible strategy for tuning the physical and chemical properties of CNTs [73], [81].

If doped CNTs are to be used as building blocks in applications, it is important to fine tune their physical properties such as wall reactivity, mechanical performance and electronic behaviour by controlling the concentration of dopant atoms inserted into the tube lattices [71].

2.5 N-doped and aligned N-doped MWCNTs for sensor applications

Nitrogen doped carbon nanotubes (N-CNTs) have become a topic of increased importance in the study of carbonaceous materials. This arises from the physical and chemical properties that are created when N is embedded into a CNT. These properties include modified chemical reactivity, modified conductivity and improved mechanical, electronic and magnetic properties [82], [83], [84]. Many studies have indicated that incorporation of nitrogen into the nanotube structures improves the electrical conductivity [85] and mechanical properties [86] of the aligned CNTs. Aligned nitrogen-doped CNTs (ACNx) are reported to exhibit excellent electro-catalytic activity

for oxygen reduction reactions (ORR) in fuel cells as metal-free electrodes [87]. Additionally, it has been found that nitrogen doping through careful control of the degree of graphitic/pyridinic nitrogen substitution improves significantly the field emission properties of CNTs [88], [89], [90] [91]. Li and co-workers reported that the rough surface of N-doped CNTs results in a larger contact area between the active layer and the electrodes in organic photovoltaic cells (OPVCs) leading to a more efficient charge collection and reduced series resistance [92]. Lu and co-workers also reported that incorporation of N-doped CNTs in bulk heterojunction (BHJ) solar cells leads to;

- enhanced light absorption of the active layer materials,
- facilitates exciton dissociation inside the active layer and
- improves charge collection efficiency of OPVCs devices [93].

Several studies have reported on the importance of vertically aligned CNTs for energy storage applications [94], oxygen reduction reactions in fuel cells [95], [96], [97], [98] and Li-ion batteries [99], [100], [101]. Besides the application of aligned MWCNTs in chemical and biological sensor applications, there is high potential for development of magnetic sensors or heterostructures with greater sensitivity and response. This calls for greater control of the catalyst impurities. Nitrogen doping of aligned CNTs has been found to modify the internal tubular structure of CNT through the formation of bamboo like confinements which can control the size, structure and geometry of the ferromagnetic impurities for sensing and magnetic data storage. This has been the subject of investigation in this work.

2.6 Role of defects in CNTs for gas sensing and solar cells applications

Defects in CNTs play a crucial role in the electronic, optical and mechanical properties of CNTs [102]. In sensor applications inherent defects in nanotubes are considered more desirable than pristine ones [103], [104] due to a stronger interaction of the adsorbing species with defects sites. The high surface-to-volume ratio, high electron mobility, great surface reactivity and high capability of gas adsorption have enabled the CNT surface to be used as the active layer in gas sensing [105].

Besides these attractive properties, the application of CNTs in commercial sensors is circumvented by the relatively poor selectivity of pristine CNTs to a variety of gases. Their use as templates provides a better strategy to increase the sensitivity and selectivity of CNTs and it is accomplished through loading on the tubular structure with transition metal oxides or chalcogenide based alloys.

To this end, alloy compounds such as SnO_2 and CuO have been embedded in or combined with CNTs for sensing applications. In their bulk form, SnO_2 and CuO have been used as gas sensors (H_2) albeit with limited surface reactivity and reduced density of the active sites. Hence the decoration of CNTs with metal oxides is anticipated to enhance surface reactivity, response and recovery times. Several reports corroborate the use of metal oxides decorated MWCNTs including SnO_2 decorated CNTs for chemical sensor applications [106], [107].

CNTs' superior charge carrier mobility and tunable work function foster their application as efficient exciton dissociation centres. These attractive features have further stimulated research towards the incorporation of CNTs into organic bulk heterojunction solar cells for efficiency and device stability enhancement [108], [92], [109], [110], [111].

Bulk CdS has been used as a component of the active layer in inorganic, and hybrid solar cells. The reported efficiencies are way lower than those of Si based solar cells. CdS decorated CNTs incorporation in solar cell have yielded low photo conversion efficiencies as reported by several researchers [112], [113]. To increase the interfacial area and match the energy levels in the hybrid solar cells requires the possible doping with nitrogen. The doping of heteroatoms such as nitrogen to CNTs can change their crystallinity and reactivity [114], [115]. The addition of nitrogen to the carbon lattice confers MWCNT n-type semiconductor properties [116]. Nitrogen creates defects in the MWCNT by forcing arrangement of the carbon atoms around the heteroatoms, thereby introducing disorder into the graphene layers and curvature of the CNTs [115]. Nitrogen incorporation can be pyridinic or pyrrolic depending on the percentage of nitrogen in the CNT and the doping conditions [117]. Since nitrogen has one additional electron as compared to carbon, it is believed that this extra electron can carry current [118].

2.7 Carbon coated GaN (C – GaN)

GaN is a wide band gap (3.39 eV) semiconductor with excellent thermal stability [119] and it crystallizes in the wurtzite structure [120]. Due to its wide-bandgap nature, excellent thermal (up to 500 °C) and chemical stability [121] have been reported. GaN has a high potential for applications in optoelectronic and electronic devices such as light emitting diodes (LEDs) [122], laser diodes [123], two-dimensional quantum wells [124], field emission transistors [125], [126] and integrated circuits [127], [128]. Among the application of interest for GaN is its use in robust sensing of chemicals, gases and radiation at high temperatures and under extreme conditions. This is evident by the spontaneous and piezoelectric polarization-induced surface and interface charges

which are currently used in the development of highly sensitive and robust sensors for gas, polar liquids and mechanical pressure detectors. Surface symmetries influence the adsorption sites and orientation of organic molecules in the first monolayer [129], [130], [131] of a device. The surface symmetry is a vital property for controlling the properties of materials as well as to understand their surface reconstruction [132]. In order to suppress leakage currents in GaN based electronic devices (e.g. in high electron mobility transistors (HEMTs) and field effect transistors (FET)) a semi-insulating buffer layer of GaN is needed as an isolating barrier between the substrate and the active region of a device [133]. Xu et al., found out that as-grown GaN layers contain residual donors [134]. Numerous research reports on the doping of GaN with carbon and the effect of this doping on the properties of GaN have indicated that the properties of GaN can be improved by addition of carbon, thus increasing its applicability. A prerequisite for successful group III nitrides application in electrically driven devices is the controllable doping with both n- and p-type dopants. While n-type doping of GaN has been achieved by many groups, doping with acceptors is still a challenge. The successful p-type doping of GaN has been predominantly achieved with magnesium [135], [136], [137]. This dopant has some drawbacks among which are its high thermal ionisation energy and its tendency to form defect structures that compete with substitutional configurations [138]. Another potential p-type dopant that has attracted much attention is carbon. Attempts have been made to intentionally incorporate carbon into GaN [139], [140], and this has been motivated by the desire to find a p-type dopant for GaN. Potential application of C doping is in the production of semi-insulating GaN for use in fabrication of high electron mobility transistors (HEMTs) [141], [142], [143], [144].

Carbon can be incorporated either on a Ga or N site in GaN. Lyons and co-workers reported that carbon is expected to be most stable when deposited on the N site (C_N) from atomic size considerations. However, the preference depends on the relative abundance of Ga and N, i.e., on the Ga and N chemical potentials as well as on the Fermi level [145]. A number of theoretical and experimental studies have reported that carbon substituted on the N site acts as a shallow acceptor [146], [147], [148], [149], [150], [151]. Wright predicted that C_N should readily form in n-type and C_{Ga} in p-type GaN as compensating species [139]. Compensation of C_N acceptors by C_{Ga} is predicted to occur in C doped GaN grown under N-rich conditions. Efforts to produce p-type C-GaN have had limited success. The difficulty of obtaining p-type conduction by carbon in a wurtzite structure may be attributed to the fact that the formation energy of the C_N is not small on the surface of a p-type material [147]. As mentioned earlier, surface symmetries influence the

adsorption sites and orientation of organic molecules [152], [153], [131] and is a vital property for controlling the properties of materials as well as their surface reconstruction [154]. Yang and co-workers have carried out experimental work on carbon-coated GaN using amorphous carbon [155] by using carbon coated GaOOH nanospindles as precursors. A common route to dope GaN with carbon is by chemical vapour deposition (CVD) and to utilize the carbon atoms on the gallium precursor, typically trimethylgallium (TMG) or triethylgallium (TEG). The incorporation of carbon from Ga precursors can be controlled by parameters such as temperature, pressure and flow rate of the Ga precursor [156], [157]. Li and co-workers reported that acetylene (C_2H_2) can be used as a precursor in carbon doping and this occurs without degrading the quality of the GaN [158].

2.8 Theoretical principles of Sensors

Human senses (sight, hearing, smell, taste and touch) are crucial in our daily activities. Our senses act by chemical or physical means and our eyes, ears etc. act as sensors and actuators whose signals are processed and measured by the brain to elicit a quantifiable response. A sensor is a device that detects a change in a physical or chemical stimulus and turns it into an electrical signal which can be measured or recorded. Sensors and actuators must be studied in an interdisciplinary approach that involves physics, chemistry, electronics, biology and agriculture. A *transducer* is a device that converts one form of energy into another. Generally, a sensing or sensitive layer/medium directly responds to an external stimulus, while a transducer converts the response into an external measurable quantity. As distinct from *detectors*, sensors are employed to monitor and quantify changes whereas detectors simply indicate the presence of an entity that is measured [159], [160]. The characteristics of a sensor may be classified as being either *static*, or *dynamic*. Static characteristics are those that can be measured after all transient effects have stabilized to their steady state. Thus for static sensors the key questions for functionality entail;

- a relative change in sensor's output response due to the stimuli, this aspect addresses the responsivity of the sensor
- the resolution of input stimuli that gives an output signal
- The temporal response of the changes in the output signal

Dynamic characteristics on the other hand describe the sensor's transient properties. These typically address questions such as; at what rate is the output changing in response to the input? and what impact would a marginal change in the input conditions induce on the transient response?

2.8.1 Parameters to characterize sensor performance

The performance of a gas sensor is characterised by various parameters such as sensor response, sensitivity, selectivity, stability, response and recovery time. When deciding what materials are to be employed as sensors for a particular gas, certain properties need to be assessed;

Sensor response S (%) is the ratio between the difference of resistance with and without the presence of gas molecules and the original resistance value of the sensor as illustrated by equation 2.1 below

$$S (\%) = [(R_g - R_{air})/R_{air}] \times 100, \quad (2.1)$$

where R_{air} is the original resistance of the sensor in air and R_g is the resistance of the sensor in the presence of a target gas [161].

Sensitivity (S) This is defined as the change of measured signals per analyte concentration unit. Normally, this value can be extracted from the slope of a calibration plot, i.e. a plot of concentration as a function of sensor response [162], [163], [164] or $S = R_{out}/R_{in}$ [165], [166], [167]. The selectivity is the capability of a gas sensor to exhibit response to a specific group of gases or to a certain gas in the presence of other gases.

The **stability** of a gas sensor is used to obtain a reliable response, which characterises the quality of a signal over a period of time [168].

The **response** and **recovery time** of a gas sensor, is measured in the range from seconds to several tens of minutes [169]. The response time is defined as time used to reach 90% of response in the presence of gases [170], [171], [172]. On the contrary, the recovery time is the time of returning to 90% of the original value in the absence of a gas [173], [174].

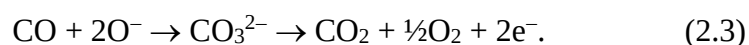
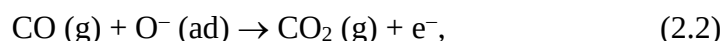
Working temperature is the temperature at which the sensor material must be heated to obtain the best optimal response.

2.8.2 Gas sensing mechanisms

The sensing mechanism in semiconductors relies on perturbations of surface conductivity induced by the interaction between target gases and the surface of the semiconductor.

2.8.2.1. Surface adsorbed oxygen ion mechanism

The sensing mechanism of metal oxide based gas sensors is related to their surface adsorbed oxygen ions. In the temperature range of 200 – 500 °C, oxygen ions such as O_2^- , O^- and O^{2-} are adsorbed on the surface of metal oxides. This will induce a negative charge on the surface [175]. Various gases adsorbing on metal oxides will interact with oxide ions and change the conductivity of the metal oxides. After exposure of a surface to a reducing gas, the surface releases a negative charge due to oxidation thereby increasing the conductivity of the metal oxides. Taking a reducing gas such as CO as an example [176]



If an electron-acceptor gas is present, it will accept the charge thereby decreasing the conductivity of metal oxides. For example



2.8.2.2. Chemiresistor mechanism

This is one of the most investigated mechanisms that is used to explain the operational principles of gas sensing devices. This type of mechanism involves the adsorption of gas molecules on the surface of the gas sensing materials leading to an induced change in the resistance of the material. By measuring the change in resistance due to adsorption allows the gas to be detected [177]. Chemiresistors have many advantages such as ease in fabrication, simplicity of operation, cost effectiveness, cyclability, low power consumption and offer advances in miniaturization [178], [179]. Chemiresistors contain a sensing material supported by an inert substrate and two metallic electrodes or interdigitated electrodes. They can be used to detect O_2 , CO, H_2 , NO_x , SO_x and some organic vapours [180], [181], [182], [183].

Sensors based on nanostructures have an advantage over the bulk counterparts due to their increased surface-to-volume ratio. Their large surface areas increase device sensitivity by offering more active sites for the analyte species. Wide band gap semiconductors such as GaN which can cover the highest occupied molecular orbitals to the lowest unoccupied molecular orbitals in bioorganic systems are favourable for bioelectronics applications [184]. Also their chemical inertness and biocompatibility is an added advantage [185]. The use of 1D group III-nitride

nanostructures in biosensors has been documented [186], [187], [188], [189]. Most importantly the use of nanostructures allow for a high density of devices on a chip to be achieved.

The primary classes of gas sensing materials are metal oxide semiconductors, CNTs and conducting polymer composites. The sensitivity of the sensors can be enhanced when the materials are at the nanoscale. Therefore, a high surface to volume ratio, which is available in nanomaterials, is suitable for this purpose. However, selectivity becomes a major setback as nano-sensors are known to possess a gas specificity weakness. Semiconducting oxides are known to present a response to various gases at elevated temperatures that are typically $>200\text{ }^{\circ}\text{C}$. GaN as a sensor does operate at high temperatures and it has to be functionalized with a metal for it to sense gases on its surface.

2.9 Solar cells

Typically there are two types of solar cells namely organic (OPVCs) and conventional inorganic photovoltaic solar cells (IPVCs). Their operating principles are almost the same. The differences arise in their photoconversion mechanism. The process of light conversion into electricity takes place in four main steps described as follows;

- absorption of a photon leading to the formation of an exciton (electron – hole pair),
- exciton diffusion to the donor-acceptor interface,
- exciton dissociation and subsequent charge transfer and
- charge carrier transport and collection [190], [191], [192]. In OPVCs there is an extra step, the charge separation step before the charge transport step. Light harvesting is carried out by an active material, in which photon absorption generates a local, generally short-lived charge separation. Charge transfer across specific contacts with a donor material able to transport positive carriers, on the one side, and an acceptor material constituting an electron transmitting medium, on the other side, prevents the charge recombination and allows the build-up of a significant photovoltage across the device. These types of solar cells do not depend on a built-in electric field at a p-n junction, but rather rely on prompt electron transfer at interfaces between materials, which energy levels are closely aligned. This illustration is shown in Figure 2.3.

The major photovoltaic steps include: photo-excitation into excitons (1), excitons migration to interfaces (2), charge transfer from the donor to the acceptor at the interface (3), charge migration to electrodes (4) and charge injections into electrodes. There are also competing processes that quench the photovoltaic conversion efficiency. These processes include the exciton recombination either at the donor or at the interfaces with trapped charge carriers (germinate recombination).

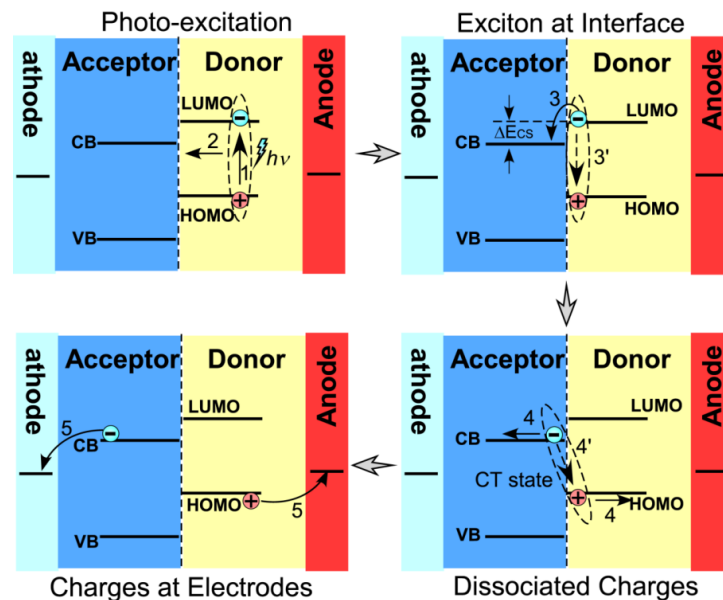


Figure 2-3: A scheme of the charge separation process at the Donor : Acceptor interface in a hybrid solar cell [193].

The difference is that in OPVCs light absorption leads to Frenkel exciton formation whereas in conventional IPVCs the electron – hole pairs are generated immediately upon light absorption [191].

Photo-absorption in inorganic PV cells is characterised by the formation of a Wannier exciton corresponding to the weakly bound electron interaction in the conduction band with the hole found in the valence band. After light absorption, inorganic semiconductors immediately produce free carriers, while organic semiconductors require additional processes to produce free carriers. Organics semiconductors form strongly bound exciton that diffuses from the donor levels into the acceptor energy band levels [194].

Donors are usually conjugated polymers, oligomers or conjugated pigments while acceptors are typically made from fullerene derivatives. These materials are classified as organic

semiconductors [57]. A schematic diagram of a typical donor – acceptor system is shown in Figure 2.3. HOMO denotes the highest occupied molecular orbital and LUMO the lowest unoccupied molecular orbital of the organic molecules. An exciton is generated in semiconductors upon photon absorption [195].

The first step is light absorption which leads to the formation of the Frenkel excitons. The excitons then diffuse inside the donor to the acceptor interface. At the interface the differences in the LUMO level of the acceptor and the HOMO level of the donor as well as the work function of the electrodes provides the sufficient electric field to split the exciton into free charge carriers. The transport of the exciton is in competition with other decay processes such as luminescence or radiative recombination to the ground state. The exponential lifetime of an exciton (τ_e) is determined by the reciprocal value of all radiative and non-radiative decay rates together. For an efficient solar cell, all excitons have to reach the photo-active interface within τ_e . Transport of the excitons occur by diffusion and the distance an exciton is able to traverse, L_e , is given by:

$$L_e = \sqrt{D_e \tau_e} \quad (2.5)$$

where D_e is diffusion coefficient of the excitons [196].

In an OPVC charges are created by photo induced electron transfer. In this process an electron is transferred from an electron donor material to an electron acceptor material with the aid of the additional input energy of an absorbed photon with energy $h\nu$. An electron donor (D) is characterized by a molecular material with a small electron affinity and vice versa an electron acceptor (A) is a material with a high electron affinity. The driving force required for the exciton dissociation is the difference between both electron affinity levels. In the photo induced electron transfer process an exciton at the D/A interface decays by creation of the charge separated state consisting of radicals cation of the donor ($D^{\bullet+}$) and the radical anion of the acceptor ($A^{\bullet-}$) [197]. The charge transport mechanism operating in OPVC is to drive charge carriers towards the electrodes. After charge transfer the electrons and holes are in close proximity, hence there is a large chemical potential gradient that drives the charge carriers away from the exciton dissociating interface.

The collection of charge carriers at the electrodes is accomplished by a transparent conductive oxide (TCO) like indium tin oxide (ITO) (cathode) on one side and a metal contact like aluminium (anode) on the other side. An ohmic contact between the electrodes and the molecular layers is formed to take the charges.

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Chapter 3: Experimental techniques

3.1 Introduction

Carbon nanotubes have received widespread research interest due to their numerous application potential since the award of the Nobel Prize to Ijima. They have been classified on the basis of the number of concentric walls or the chirality of the graphite like lattice. As such literature on these allotropes of carbon has shown that their electronic properties span between semiconductor and metallic like behaviour with ballistic form of charge transport. More recently the growth of large area single layer graphene like structures have attracted enormous research interest as the presence of defects could lead to the tuning of the optoelectronic properties. In the field- and photo-emission for display devices, aligned carbon nanotubes, doped or otherwise, are intensively investigated for large area devices with high electron emission yield.

Several techniques on the synthesis of N-CNTs have been reported in the literature [1], [2], [3], [4], [5], [6]. These techniques include arc-discharge, laser ablation, chemical vapour deposition (CVD) and autoclave systems. In this study, two procedures have been used to fabricate N-CNTs nanomaterials namely;

- the horizontal CVD method, and
- the spray pyrolysis method.

All these methods produce diverse multiwall CNTs. However the production of N-CNTs require the use of a catalyst source, a carbon source and a nitrogen source. In this work, organometallic complex, es (Fe-Co/CaCO₃ and ferrocene) were studied as catalysts for N-CNT production and the ferrocene was dissolved in an appropriate organic solvent such as toluene. In the sections below, the different methods are briefly described but more specific details for each method is given under the experimental section of each chapter in this thesis. Characterization of the N-CNTs and the loading of metals on them was carried out using conventional characterization techniques as explained in section 3. Additionally, N-CNTs decorated metal oxides were synthesised using thermal decomposition route.

3.2 Materials

All the materials (reagents and gases) were used as purchased. All reagents were commercially available from Sigma Aldrich chemicals and were used without further purification. Gases were available from AFROX and the gases used were: nitrogen (99.999%), argon (99.999%) argon (95%) and hydrogen 5%, acetylene and ammonia (99.999%).

3.2.1 Catalyst Preparation

The Fe-Co/CaCO₃ catalyst was prepared by an impregnation route using an aqueous mixture of Fe(NO₃)₃·9H₂O and Co(NO₃)₂·6H₂O [7]. The two metal nitrates (purchased from Sigma-Aldrich) were of analytical reagent grade and were subsequently used without further purification. Calculated amounts of the metal nitrates were mixed and dissolved in distilled water to make a 0.3 M Fe-Co (50:50 w/w) precursor solution. This precursor solution was added dropwise to the stirred CaCO₃ and the mixture was left to stir for 30 minutes. The resulting metal support mixture was then filtered and dried in an oven at 120 °C for 12 hours (to completely remove the nitrates), and thereafter cooled to room temperature. The resulting mixture was then ground and sieved using a 150 µm mesh sieve. Calcining of the powder was carried out at 400 °C for 16 hours in air to decompose the nitrates in the catalyst. The total loading of the Fe-Co catalyst on the CaCO₃ was 5 mass %. Mhlanga and co-workers have characterized these catalysts using different techniques [7].

3.3 Synthesis and fabrication of functional nanomaterials

3.3.1 Nitrogen-doped Multiwall Carbon nanotubes (N-CNT) by horizontal CVD

Nitrogen-doping of multiwalled carbon nanotubes (N-CNT) was done by the decomposition of acetylene (C₂H₂) (Afrox) over a 5% Fe-Co bimetallic catalysts supported on CaCO₃ [7] at 850°C for 45 mins. In a typical procedure 250 mg of catalyst (Fe-Co/CaCO₃) in a quartz boat (120 mm × 15 mm) was placed in the centre of a quartz tube (51 cm × 1.9 cm) in a horizontal programmable furnace. The furnace was electronically controlled to accurately provide the desired heating rates (±1°C), reaction temperature and gas flow rates. The CVD setup used is shown in Fig 3.1. The

catalyst was spread to form a thin layer in the quartz boat. The furnace was then heated at $10\text{ }^{\circ}\text{C min}^{-1}$ under a continuous flow of nitrogen gas (N_2) (Afrox) (240 mL min^{-1}). Once the desired temperature was reached ($850\text{ }^{\circ}\text{C}$), the N_2 (240 mL min^{-1}) and C_2H_2 (90 mL min^{-1}) were simultaneously bubbled through acetonitrile (CH_3CN) at room temperature into the furnace for nitrogen doping to take place [8]. The reaction was allowed to take place for 45 minutes. After this, the bubbling of the gases through CH_3CN was stopped and the system was left to cool down to room temperature under N_2 (240 mL min^{-1}). The quartz boat, the carbon deposit and the weighed catalyst were removed from the reactor.

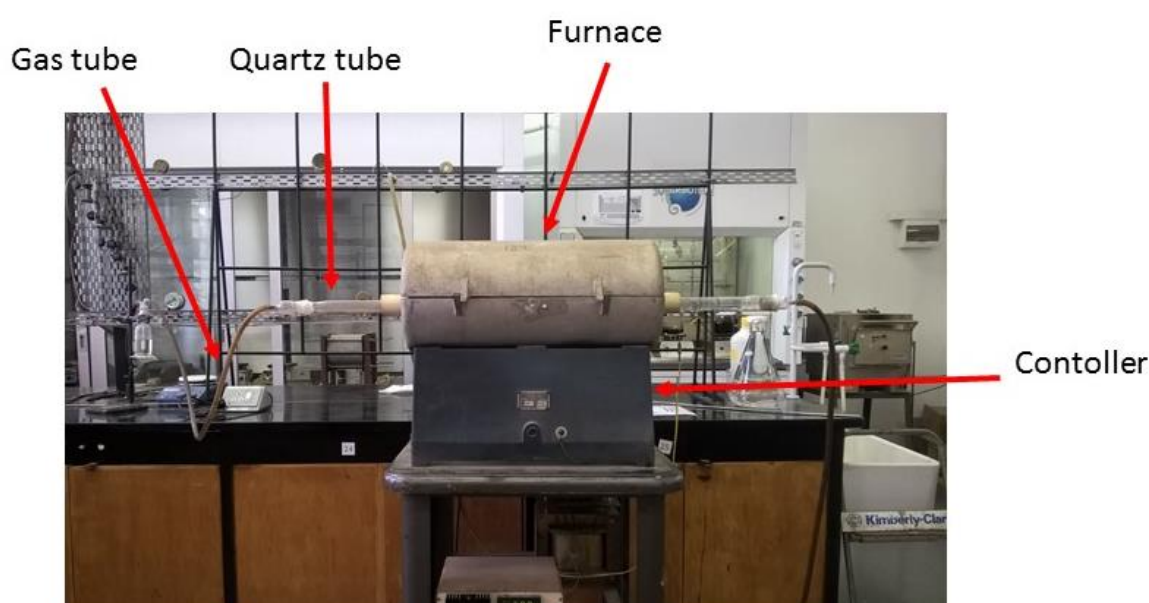


Figure 3-1: Horizontal Chemical Vapour Deposition set-up for N-CNT synthesis

3.3.2 Aligned Nitrogen-doped Multiwall Carbon nanotubes (N-A-CNT) by Spray pyrolysis CVD method

Aligned nitrogen doped MWCNTs (N-A-CNT) were synthesized using a spray pyrolysis procedure also referred to as Aerosol Assisted Chemical Vapour Deposition (AACVD) similar to that reported in literature [9]. The liquid feed (consisting of catalytic precursor and hydrocarbon source) is continuously supplied into the reactor for two principle reasons, namely;

To engender the formation of the catalysts,

To simultaneously promote the nucleation and the growth of carbon nanotubes (CNTs) throughout the reaction period [10].

Toluene and acetonitrile were used as purchased (Sigma Aldrich and Fluka). Approximately 2.50 g of ferrocene as a catalyst was dissolved in 50 mL solvent (50 mL toluene, 50 mL of 1:1 toluene/acetonitrile, 50 mL acetonitrile). The samples were coded as follows, N-A-CNT_x, with x representing the volume ratio of toluene to acetonitrile in the mixture, such that:

- N-A-CNT₀ where x = 0 refers to the sample made with toluene,
- N-A-CNT_{0.5} for samples made with 1:1 toluene/acetonitrile volume ratio
- N-A-CNT₁ for samples made with acetonitrile.

The precursors were nebulized using a 1.45 MHz oscillator and the carbon source was carried into a quartz tube (800 mm × 28 mm), placed in a furnace which was maintained at 850 °C. A quartz boat (120 mm × 15 mm) was placed at the centre of a quartz tube. The average droplet size for the solvents is ~2.2 μm at 1.54 MHz [11]. Ultra-pure argon (Ar) and 5% hydrogen (H₂) in Ar gas purchased from Afrox were used as the carrier gases and the gas flow rate was controlled using unit mass flow controllers. The furnace was heated to the target temperature at 10 °C min⁻¹ in pure Ar ambient maintained at a flow rate of 400 mL min⁻¹. After the desired temperature was reached, the Ar (400 mL min⁻¹) and 5% H₂ in Ar (100 mL min⁻¹), were simultaneously allowed to bubble through the solvent, and after nebulizing the solution was carried into through the quartz tube. The pyrolysis was carried out for 45 min. Following the reaction, the pure Ar gas was allowed to flow directly through the reactor without passing through the solvent while the 5% H₂ in Ar gas was switched off. The furnace was then allowed to cool to room temperature. The yields were determined by scraping the products from the quartz boat as well as the quartz tube wall and weighed. Trends are readily detected in the series of reactions performed and errors of ca. 10% can be expected in the determination of the yields. The experimental setup used for the synthesis of A-CNT_x is presented in Figure 3.2 and properties under investigation presented in detail in Chapter 5.

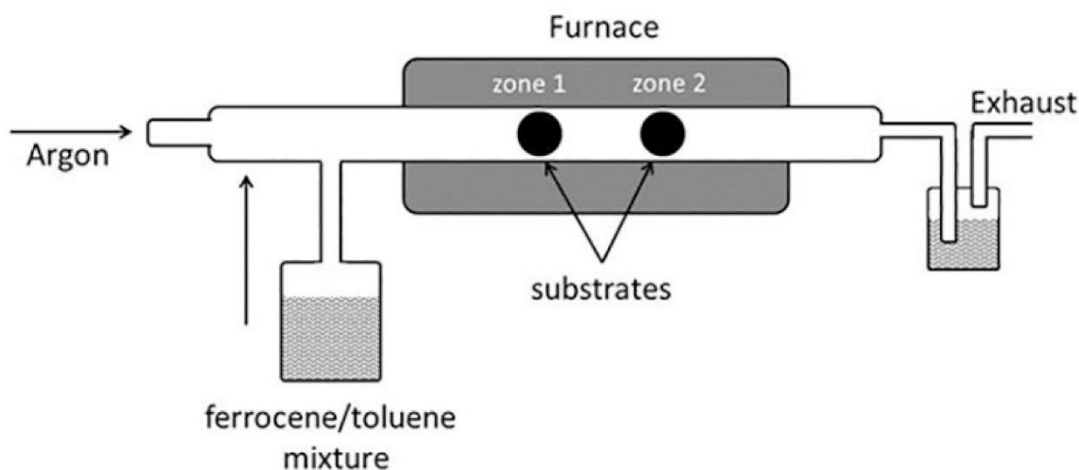


Figure 3-2: AACVD schematic diagram: Adapted from C. Mercado-Zúñiga et al., Materials Research. 2016; 19 (Suppl. 1): 52-58 [12].

3.4 Purification of N-CNT and A-N-CNT_x

The samples were purified using 55 % HNO₃ under reflux in an oil bath held at 110 °C for 6 hours to remove the residual catalyst and to introduce oxygen surface groups on the CNT surface. The acid-treated carbon materials were then filtered and washed several times with distilled water until the pH of the filtrate was neutral. The nitrogen-containing materials were dried at 120 °C for 12 hours. The CaCO₃ support as well as catalyst particles (Fe-Co and Fe from ferrocene) were removed without affecting the CNT wall structures. Some residual material (~3 %) appears to be left behind after the washing. The purified samples are denoted as N-CNT and N-A-CNT_x are now ready for use.

3.5 Loading of metal oxides and sulphide on N-doped Carbon nanotubes (N-CNT)

3.5.1 SnO₂ on N-CNT (N-CNT_SnO₂)

The procedure of loading SnO₂ on CNT was carried out by foremost dissolving 4.0 g of hydrous SnCl₂·2H₂O in 150 ml of distilled water and thereafter adding 2.0 ml of concentrated HCL (32%) to the mixture. The mixture was sonicated for 15 mins after which 200mg of purified N-CNT was

added, while continuously stirring the solution for 2 hours at room temperature. Finally, the sediments were filtered and washed completely with distilled water and then dried in air at 100 °C overnight. The final product was calcined at 500 °C for 2 hours (N-CNT_SnO₂) [13].

3.5.2 CdS on N-CNT (N-CNT_CdS)

For the loading of CdS; 3.025 g of Cd(CH₃COO)₂·2H₂O and 0.951 g of Thiourea were dissolved in 70 ml of diethylene glycol (DEG). Subsequently 200 mg of N-CNT was then added into the solution and sonicated for 30 minutes. The obtained black product was then heated to 180 °C and kept at this temperature for 2 hours. After cooling down to 25 °C, the product was mass separated via centrifugation at a speed of 3500 rpm for 15 minutes. Finally, the sediments were filtered and washed twice with absolute alcohol to completely remove DEG. The resulting mixture was dried at 100 °C for 12 hours (N-CNT_CdS) [14]. The characterisation of these loaded N-CNT materials is explained in detail in subsequent chapters.

3.6 Synthesis of GaN and carbon coated GaN (C-GaN)

GaN nanostructures (NSs) were synthesized using a CVD method in a single stage furnace (see Figure 3.1). The synthesis of GaN in a single stage furnace usually requires higher temperatures (> 1000 °C). A measured amount of Ga₂O₃ powder was placed in a boat which was subsequently placed in the centre of a quartz tube enclosed by a heating furnace. Pure nitrogen gas (N₂) (purchased from Afrox) was allowed to flow through the quartz tube at a flow rate of 30 mL/min while heating the furnace to 1100 °C. When the desired temperature was reached, ammonia gas (NH₃) (Afrox) was introduced at a flow rate of 50 mL/min while N₂ was kept at the flow rate of 30 mL/min. After 45 minutes, the NH₃ was switched off and the furnace was allowed to cool down to room temperature while N₂ was allowed to pass through the furnace. When the furnace has cooled down to room temperature, the boat was removed and its content weighed to establish the amount of the as-synthesised GaN formed [Kente, T. (2013) *Synthesis and Functionalization of Gallium Nitride Nanostructures for Gas Sensing and Catalyst Support* PhD Thesis University of the Witwatersrand, 2013].

3.6.1 Carbon-coated GaN (C-GaN)

As-synthesised GaN nanostructure powder was placed in a boat and placed in the centre of a quartz tube. Pure N₂ or argon (Ar) (Afrox) was allowed to flow at a rate of 80 mL/min through the quartz tube at a while heating the furnace to 600 °C. Upon reaching the desired temperature, acetylene (C₂H₂) (Afrox) was introduced at flow rate of 80 mL/min while fixing the N₂ flow rate constant at 80 mL/min. After 45 mins, the C₂H₂ was switched off and the furnace allowed to cool down to room temperature in N₂ ambient. When the furnace has cooled down to room temperature, the boat was removed and its content weighed to establish the amount of C-GaN formed (C-GaN CN (carrier gas N₂) and C-GaN CA (carrier gas Ar)). The experimental setup is shown in Figure 3.3.



Figure 3-3: Experimental setup for C-GaN synthesis.

As-synthesised GaN nanostructure powder was placed in a boat and placed in the centre of a quartz tube. Pure Ar or N₂ gas was allowed to flow through the quartz tube at a flow rate of 80 mL/min while heating the furnace to 600 °C. When the desired temperature was reached, the Ar or N₂ gas was allowed to pass through toluene in a bubbler at the same flow rate of 80 mL/min. After 45 minutes, the bubbler was switched off and the furnace was allowed to cool down to room

temperature while Ar or N₂ was allowed to pass through the furnace at the same flow rate. When the furnace has cooled down to room temperature, the boat was removed and its content weighed to establish the amount of C-GaN formed (C-GaN TA (Ar as carrier gas) and C-GaN TN (N₂ as carrier gas)).

3.7 Characterization

3.7.1 Structural properties carbon based nanostructures

X-ray diffraction is a useful technique to provide detailed information on the nature of the phases present in materials. These phases may either have a crystalline or amorphous footprint. In this work, Powder X-ray diffraction (PXRD) has been used to identify the structural phase of all the materials of interest using a Bruker D2 Phaser with Co-K α (1.789Å) radiation. The samples were finely ground and loaded on standard substrate holder which provide for controlled sample height displacement relative to the incident X-ray beam. The data was collected in the continuous θ - θ geometry from $\sim 10^\circ$ to 90° based on the Bragg-Brentano geometry. The Debye Scherrer [15] and the Williamson-Hall formalisms were used to calculate the particle size and micro strain in the powder materials investigated in this work.

3.7.2. Phase determination by Powder X-ray diffraction (PXRD)

The prepared powder samples were placed into the circular cavity of a silicon single crystal wafer zero background sample holder as shown in Figure 3.4.

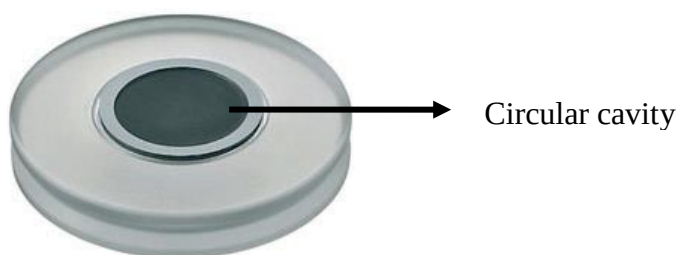


Figure 3-4: Zero background sample holder.

The sample was evenly and randomly distributed on the sample holder using a glass slide. The sample holder with its contents was then inserted into the Bruker D2 Advance diffractometer [Bruker D2 diffractometer from Bruker AXS GmbH, Germany] as shown in Figure 3.5 and the

subsequent X-ray analysis was done. The acquisition times were in the order of 10 minutes for powder crystalline samples. Powder X-ray diffraction (Bruker D2 Phaser) with Co-K α (1.789Å) radiation was used to identify the structural phases present in our samples.



Figure 3-5: Bruker D2 Advance diffractometer.

3.7.3 Thermal properties and stability by Thermogravimetric analysis (TGA)

The thermal stability of the samples were investigated by thermal gravimetric analysis (TGA) instrument conjugated with a weight loss derivative curve (DTG) using a Perkin Elmer Pyris 1 TGA. For each sample, a 10 mg was placed in a ceramic pan in the instrument's furnace. The sample was heated from room temperature to 900°C at a rate of 10°C/min under air (10 mL/min) and the data on the weight loss was collected. The weight loss plot (TGA) provides information on the thermal stability, nature and composition of the samples. The derivative curve provided information of the weight loss as a function of temperature. A typical TGA measurement is presented in Figure 3.6 in which the weight loss dependence with temperature is illustrated.

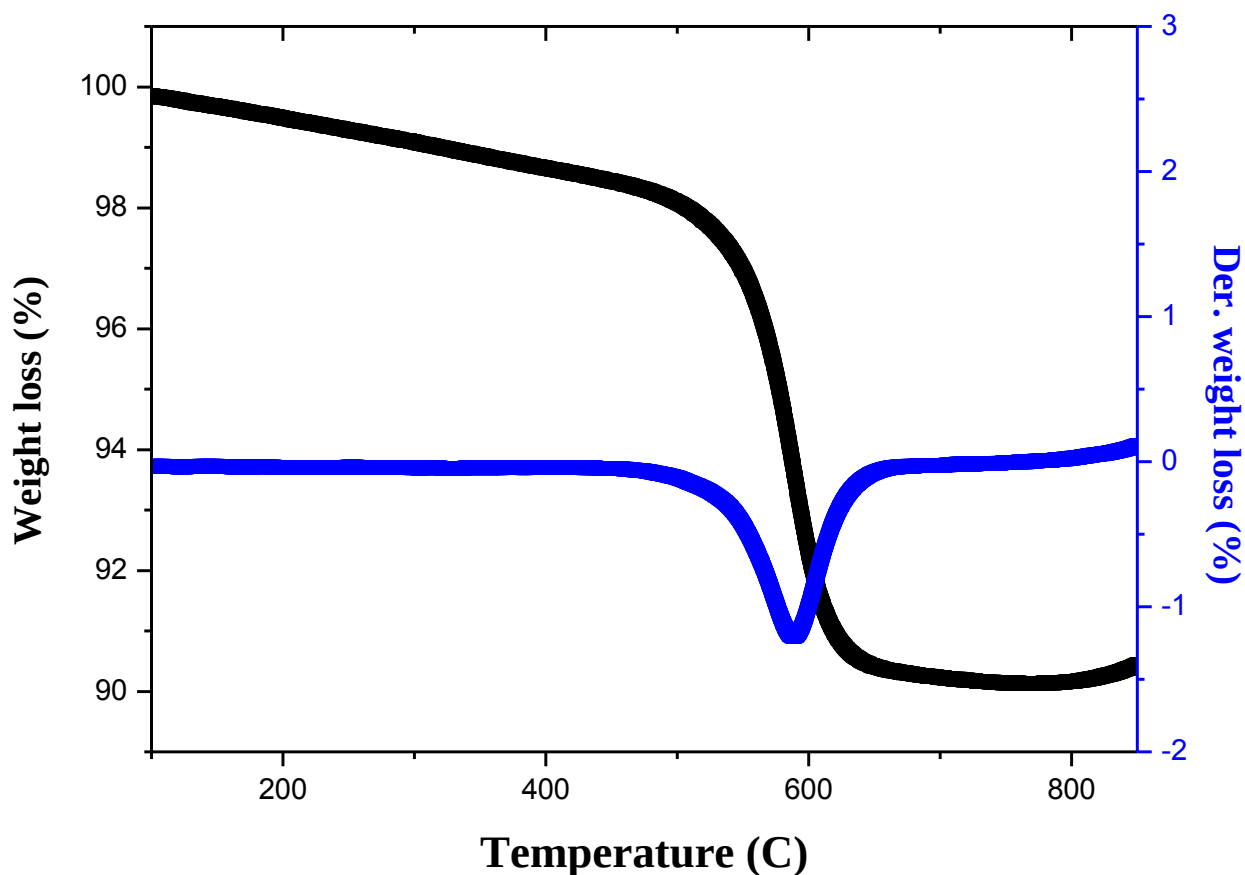


Figure 3-6: TGA profile (black) showing the weight loss and the derivative (blue) to

3.7.4 Morphological studies

3.7.4.1 Transmission electron microscopy (TEM) analysis

The morphological features of the synthesized N-CNTs and C-GaN nanostructures were ascertained by TEM using a FEI Technai G2 spirit electron microscope operating at 120 keV. A sample specimen was prepared by dispersing a small amount (≈ 2 mg) of the purified sample in ethanol (1 mL) and the mixture sonicated to form a homogeneous solution. A few drops of the homogenous solution were placed onto a carbon coated copper grid and the grid dried in ambient air for 30 min before inserting it in the microscope. The grid was placed on a single tilt sample holder and the holder was inserted into the TEM (Figure 3.7). When the sample was in place, a good vacuum has been created, the beam was turned on and the column valves were opened the sample was ready to be viewed. The diameters of the samples images obtained were measured using Image J 1.48v software. The diameters of 100 randomly chosen spots were measured per sample.



Figure 3-7: FEI Tecnai G2 Spirit electron microscope.

3.7.4.2 Scanning electron microscopy (SEM) analysis

The morphology of the obtained samples was determined using a FEI Nova Nanolab 600 FIB/SEM. A small amount (≈ 2 mg) of the sample was evenly spread on a carbon tape placed on a carbon stab. The homogeneously dispersed sample on the carbon tape was coated with a palladium/gold coating for 2 min to make it conductive. The stab was then placed in a SEM and images captured at 5 keV.



Figure 3-8: JEOL 7500F scanning electron microscope used to study the samples.

3.7.5 Raman spectroscopy

Raman spectroscopic analysis is an important tool to determine the degree of graphitization and the structural properties of materials. For the samples in this work, the Jobin-Yvon T6400 micro-Raman spectrometer equipped with a laser excitation wavelength of 514.5 nm and a liquid N₂ cooled charge coupled device (CCD) detector was used. The obtained vibration modes were deconvoluted using Lorentzian functions in Origin 8.50 professional package to measure peak positions and intensities after background correction. All the measurements were carried out at room temperature.

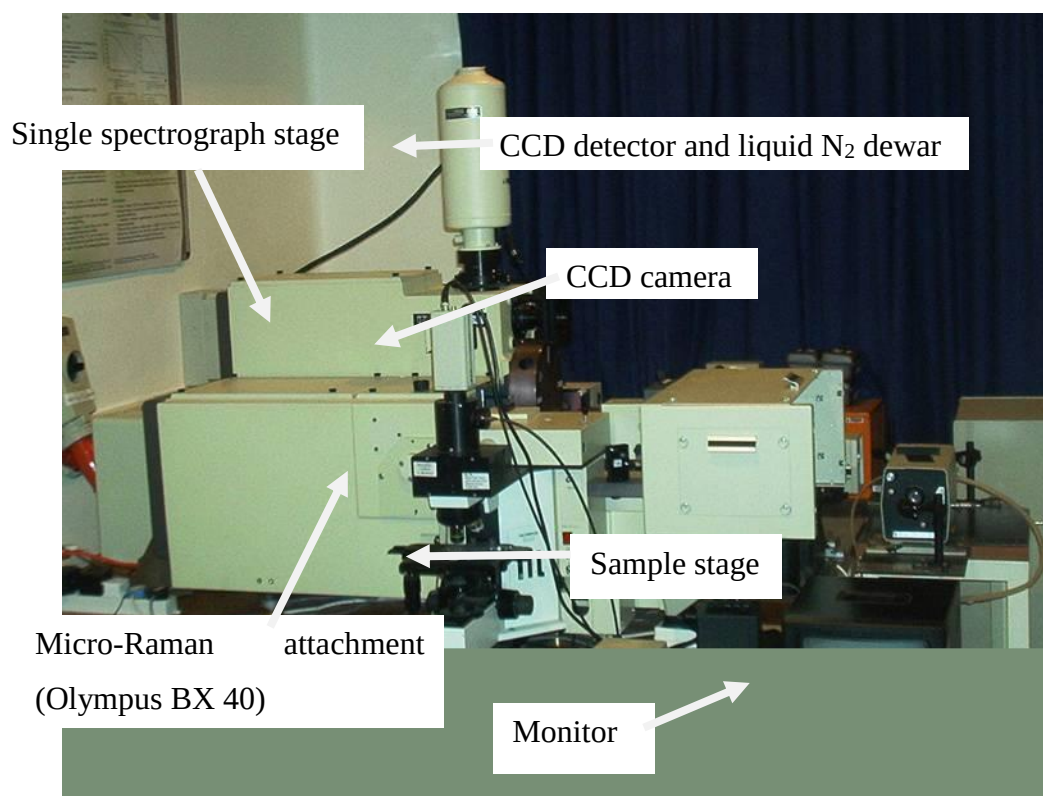


Figure 3-9: Raman Spectrometer set-up for room temperature measurements.

3.7.6 Brunauer Emmett Teller (BET) surface area analysis

Before taking the measurements, the samples were degassed at 200°C for 4 h in N₂. The N₂ adsorption and desorption isotherms of the samples were taken using a Micromeritics Tristar 3000 instrument at 77K. The specific surface area was calculated by the BET method from N₂ adsorption data and the Barrett-Joyner-Halenda (BJH) method was used to determine the pore size distributions calculated by analysing the desorption branches of the N₂ isotherms.

3.7.7 Photoluminescence

The optical properties were determined by photoluminescence (PL) spectroscopic studies where the data was acquired using a 244nm laser (Lexel Model 95 SHG argon ion laser) and a Horiba LabRAM micro-Raman instrument with a 150 lines/mm grating and a liquid nitrogen cooled CCD detector. Photoluminescence is the re-emission of light after absorbing a photon of higher energy and it's a radiative recombination process among excited charge carriers, such as electrons/holes

or Wannier excitons in a semiconductor during an external optical/radiative excitation process [16], [17].

3.7.8 X-ray photoelectron spectroscopy (XPS) analysis

Nitrogen doping in carbon based nanostructures can exist in three possible configurations. These configurations are pyridinic-like, pyrrolic-like and graphitic/substitutional [18] and are very difficult to determine using conventional techniques such as Energy dispersive spectroscopy or Rutherford backscattering. XPS is an optimal spectroscopic tool of choice in the determination of elemental composition and their bonding configurations of materials. The nitrogen content and configuration was determined by X-ray photoelectron spectroscopy (XPS – ThermoFisher scientific ESCALAB250Xi microprobe) that provided an Al K α source of diameter 900 μ m. The setup is equipped with an energy analyser of wide and narrow pass energies of 100eV and 20eV respectively. The sample(s) were analysed as received.

3.7.9 Mössbauer spectroscopy

The magnetic behaviour of the A-CNT samples were determined by Mössbauer spectroscopy. The Mössbauer equipment basically consists of a source (^{57}Co) in a rhodium matrix as a source of gamma rays (γ -rays), a drive mechanism for producing a Doppler velocity and a Kr-CO₂ detector which recorded the transmitted gamma rays. The spectra were obtained with a constant acceleration and were collected over 1024 channels. A commercial Personal Computer Analyzer (PCA) controller card was used for waveform generation, energy discrimination and multi-channel scaling. The discriminator allows for the selection of 14.4 keV peak. The dwell time is 100 μ s per channel. The setup is shown in Figure 3.10.

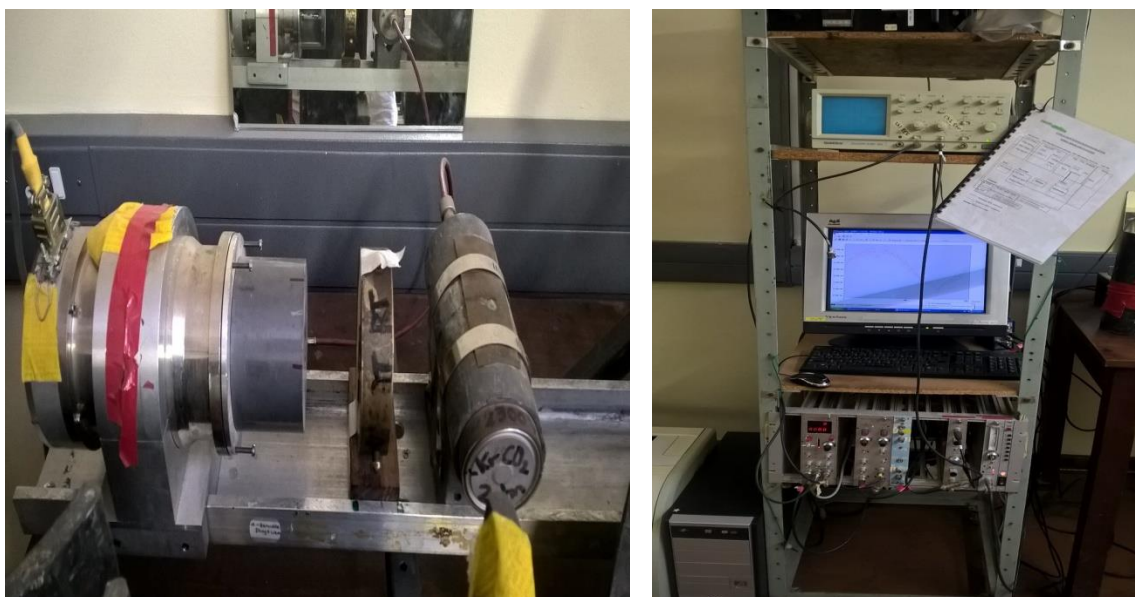


Figure 3-10: Mössbauer Spectrometer set-up comprising of the detector, drive mechanism and the electronic control

The Mössbauer spectrum is a record of the transmission rate of the resonant γ -rate, as a function of Doppler velocity between the source and the absorber. By mounting the source on a mechanical *constant-velocity* drive the total number of counts can be registered in a *fixed time*, at constant velocity, and subsequently re-measured at different velocities. The *multi-channel analyzer* (MCA) employed as data-storage, is *synchronized with vibrator sweeps*. A square wave from the multi-channel analyzer with leading edges at 1024 channels is integrated to give a systematic triangular signal.

3.7.10 Hyperfine measurements by Mossbauer spectroscopy

From the resulting powder samples 35 mg was weighed and mixed with cremora milk powder (dilutant) to achieve a uniform loading across the absorber holder. The mixture was then placed in a copper powder-clamp sample holder, 1.5 cm in diameter. The sample in the form of powder is spread uniformly and sandwiched between the two mylar windows and clamped. There should be no gap or pin-holes. The ^{57}Fe spectra were acquired using 35 mg of the samples measured at room temperature. A ^{57}Co in Rh matrix source of strength ~ 20 mCi was used in the Mössbauer measurements. The velocity scale was calibrated by means of an Fe foil of 12 μm thickness (≈ 10

mg/cm² of Fe), with Normos-90 software [Normos-90 software from Wissel Instruments, Germany] used for the analysis.

During the acquisition of the Mössbauer spectra 35 mg of material was used amounting to thickness of 20.6 – 26.5 mg/cm² of material. For a single line 5 mg/cm² of Fe is required. For a doublet, resonance is distributed between the two lines which means 10 mg/cm² of Fe may be used and for sextet it requires 30 mg/cm² of Fe. This quantity of material was used because the count rate and resonance effect (intensity) are functions of the absorber thickness in a spectrum. For a reliable analysis of spectra, determination of the thickness of the absorber is very important. If the absorber is too thick there will be too much electronic absorption, and also extrinsic broadening of the linewidths [19]. The size of the absorbers is inversely proportional to the iron concentration in the sample. Choosing an appropriate optimum thickness for the sample is vital where the iron concentration is low [20]. In this case there is a high proportion of heavy elements or the M_{fe} -value is small (M_{fe} being the mass fraction of the heavy element). The mass absorption coefficients are given as a function of wavelength on X-rays and have been tabulated at 14.4 keV for all elements by [19]

Transmission ⁵⁷Fe Mössbauer measurements were carried out at room temperature (300 K) on the CNTS with a 20 mCi ⁵⁷Co (Rh) source. Each spectrum was collected for approximately two weeks to obtain data with good statistics (~10⁷ pulses per channel). The spectra were fitted using the Lorentzian model with two sextets, one quadrupole split doublet and a single line. The data were analysed using the spreadsheet based tool Vinda developed by Gunnlaugsson [21]. Isomer shifts are given relative to an α -Fe foil (thickness of 12.5 μ m and 99.99% of purity).

3.7.11 Magnetic properties by SQUID Magnetometer

The magnetization measurements were performed with a DC SQUID (Superconducting Quantum Interference Device) magnetometer Quantum Design MPMSXL (Magnetic Properties Measurement System) in the temperature range between 2 K and 400 K.

A SQUID Magnetometer of the type Quantum Design MPMSXL is a helium cryostat with a superconducting magnet. The helium gas controls the sample temperature. The SQUID detector (which is a Josephson contact loop) is at the core of the apparatus and the measured quantity is the

electronic magnetic dipole moment μ of the sample with respect to the direction parallel the applied magnetic field.

In order to investigate the magnetic properties of a sample, it is exposed to the field of a superconducting magnet and gradually moved through a pick-up coil system. The pick-up coil system is essentially an arrangement of induction coils. The coils are wound in a configuration in which the upper and lower single turns are counter wound with respect to the two-turn centre coil. This is so as to reject interference from nearby magnetic sources. A magnetized sample induces a voltage at each step while passing the coil arrangement stepwise. The SQUID detector measures the induced voltage. The sensor is a superconducting ring which has weak-links. At these positions the critical current is significantly reduced. The magnitude of the DC current, which is proportional to the number of magnetic flux quanta is a measure of the change of the magnetic flux density caused by the magnetization of the sample as it moved through the pick-up coil system. The voltage can be plotted as a function of the sample position if the SQUID voltage is read at a large number of points. A set of such data is called the SQUID response. The SQUID response is fitted using the MPMSXL software to yield the sample magnetization. A schematic diagram of a MPMSR is shown in Figure 3.11.

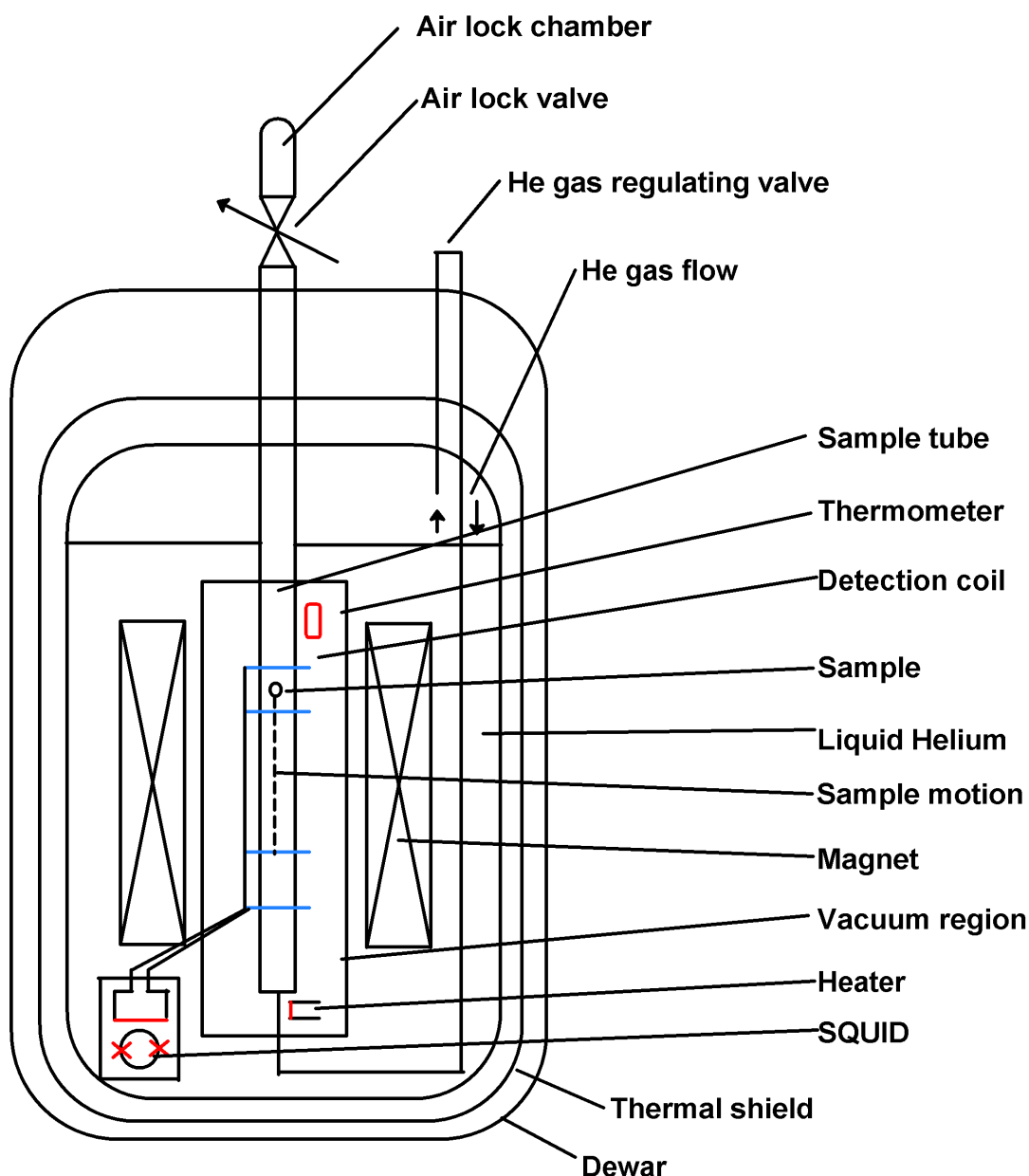


Figure 3-11: Schematic diagram of a MPMSR. Adapted from L. Fagaly, Review of

3.7.12 Magnetization measurements using SQUID magnetometer

The samples (powder) were placed in a plastic sample holder with a small amount of grease to ensure that the sample material was stationary during the measurement. This plastic sample holder was inserted into a transparent pipe (3.5 mm inner diameter) and inserted into the Magnetic Properties Measurement System (MPMS). The sample was centred in a 500 Oe and the measurement was performed using a field cooled protocol (0.5 K/min with the same measurement

interval frequency of 0.5 Hz with 3 cycles per scan). The $M(H)$ curves collected in a standard manner with the initial magnetization followed by a full loop.

The sample is glued to a straw sample holder consisting of a straw. Sample is mounted into a small fold of straw mounted in turn in the centre of the length of the straw holder. The sample holder and its content is then inserted into Fiber optic of about 2 m in length. The sample is exposed to the field of a superconducting magnet and gradually moved through the pick-up coil system (this is essentially induction coils). The sample is magnetized by a constant magnetic field and the magnetic moment of the sample is measured, producing a direct current (DC) magnetic susceptibility. For all the magnetization measurements a sample of mass of between 20 and 50 mg was used.

3.7.13 Electron Paramagnetic (Spin) Resonance (EPR)

Electron paramagnetic resonance (EPR) spectroscopy is used to determine the behaviour of individual spins present in the samples, with an emphasis on the interaction between localised spin and carrier spin states. The EPR data were recorded at room temperature using a Bruker ESP300E plus X-band spectrometer with 100-kHz field modulation and phase-sensitive detection by varying the magnetic field in the range 3400 to 3500 mT. The samples were placed in NMR tubes and the standard continuous wave technique was used to obtain all the derivative spectra.

3.8 Device fabrication and measurements

3.8.1 Fabrication of the C-GaN device

As-synthesised GaN nanostructure powder was placed in a boat and placed in the centre of a quartz tube. Pure N_2 or Ar (Afrox) was allowed to flow at a rate of 80 mL/min through the quartz tube at a while heating the furnace to 600 °C. When the desired temperature was reached, acetylene (C_2H_2) (Afrox) or the pure Ar gas was allowed to pass through toluene in a bubbler at the same flow rate of 80 mL/min was introduced at flow rate of 80 mL/min while fixing the N_2 flow rate constant at 80 mL/min. After 45 minutes, the C_2H_2 or the bubbler was switched off and the furnace allowed to cool down to room temperature in N_2 /Ar ambient. The boat was removed after attaining

room temperature and its content weighed to establish the amount of C-GaN formed (C-GaN CN (carrier gas N₂) and C-GaN TA (carrier gas Ar)).

3.8.1.1 Measurement of the gas-sensing performance

The gas sensing response of the C-GaN device was measured using a gas sensing station KSGAS6S (KENOSISTEC, Italy). The nanoparticles were ultrasonically dispersed in ethanol and drop-coated on alumina sensing substrates. The device had a Pt electrode on top surface and a micro-heater at the bottom surface. The sensor material was deposited on the interdigitated Pt electrode structure by drop-coating. The deposited layer was dried at 60 °C for 2 hrs to remove the organic solvent prior to the measurements. The sensor temperature was set at 25 and 250 °C using an applied heater voltage of 0.5 V. Various concentrations of the target gas were obtained by varying the flow rates of a mixture of target gas and dry air. The conduction or resistance response of the device to the various concentrations (5, 10, 20, 40, 60, 80 and 100 ppm) of targeted gases was measured by a Keithley 6487 pA/voltage source meter. The Keithley 6487 pA/voltage produced a voltage sweep which measured the resulting current. It also provided both sweeping and biasing. The response and recovery of the device were also measured. Figure 3.12 (top) shows the device and Figure 1(bottom) an example of the sensor substrate (UST Umweltsensortechnik GmbH, Germany) similar to the one used in the sensing measurements.

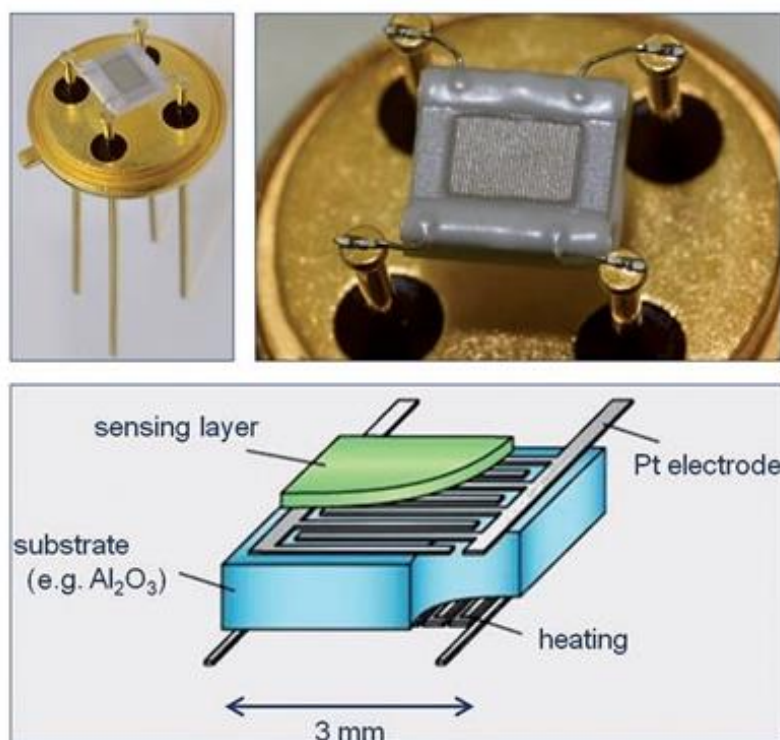


Figure 3-12: (top) the device and (bottom) an example of the sensor substrate similar to the one used in the sensing measurements [23].

3.8.2 Solar cell characterization

The fabricated solar cell devices were characterized by optical spectroscopy (UV-visible absorption spectra (UV-Vis), photoluminescence (PL) spectroscopy, Raman spectroscopy and current density-voltage (J-V) graphs.

3.8.2.1 Device fabrication for efficiency characterization

Indium tin oxide (ITO) coated glass (Merck; the resistivity of the glass was 10 Ω/cm^2). The devices were fabricated on indium tin oxide (ITO)-coated substrates. The ITO coated glass was cleaned in an ultrasonic bath containing distilled water-acetone-ethanol solutions and the residual solvent was removed by a stream of nitrogen gas. A hole transporting layer, PEDOT:PSS was then spin coated onto the ITO coated glass substrate at 2000 rpm at 60 °C for 10 mins. The resulting film

was dried on a hot plate at 100 °C for 15 min to remove any residual water. CdS nanoparticles material by weight (5, 10, 15 and 20 mg) were mixed with 10 mg of P3HT (Sigma Aldrich 90%, regioregular) and dissolved in 1 ml of chlorobenzene. The mixture solution containing CdS, P3HT (P3HT:CdS) and the chlorobenzene were magnetically stirred for 3 hours at 40 °C on a hot plate. The P3HT:CdS layers (200 nm) (with the following ratios of P3HT:CdS 0.5:1, 1:1, 1.5:1 and 2:1) was spin-coated from their corresponding chlorobenzene solutions at 2000 rpm and further annealed at 50 °C for 10 min, followed by thermal evaporation of an aluminum electrode. Aluminium top electrodes (100 nm) were deposited by thermal evaporation.

3.8.2. 2 Optical spectroscopy on hybrid solar cells

Optical absorption measurements of the film blends were made using a Cary 500 UV–visible spectrometer. The measurement were performed in the range 300-800nm. A Horiba LabRAM HR Raman spectrometer equipped with an Ar ion laser (514.5 nm) and a laser power of 0.4mW was used to examine the vibration modes and the structural order of the active layer. Photoluminescence measurements were carried out using a Horiba LabRAM HR spectrometer at an excitation wavelength of 458 nm to establish the nature of the electronic transitions after incorporation of the inorganic component in the active layer.

3.8.2.3 Current density–Voltage characteristics for photo-conversion efficiency determination

The current density–voltage (J–V) characteristics were obtained using a HP 4141B source measure unit under 100mW/cm² illumination (AM 1.5G). All the measurements were carried out at room temperature under standard conditions. The current density–voltage (J–V) characteristics were obtained using a HP 4141B source measure unit under 100 mW/cm² illumination (AM 1.5G) generated with a Newport Xenon-lamp solar simulator. All the measurements were carried out at room temperature under standard conditions. The performance of the devices was not compared to a standard reference device.

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Chapter 4: Characterization of nitrogen doped multi-walled carbon nanotubes loaded with SnO₂, CuO and CdS

4.1 Introduction

Pristine carbon nanotubes are chemically inactive and this prevents the formation of chemical bonds with most molecules [1] due to their strong sp² bonding in a near perfect hexagonal network. Several methods of modifying a CNT surface by functionalizing, doping or coating, have been suggested to further improve the properties and optimize the use of CNTs in various applications [2], [3], [4]. Carbon nanotube reactivity can be improved by functionalising their sidewalls with chemical groups [5], or by coating or filling the pristine nanotubes [6]. Surface modification of CNTs tends to increase the performance of CNT/metal oxide composites and increases not only their stability but also their electrochemical activity. Acid treatment as a chemical functionalization method creates carboxylic acid and hydroxyl groups on the surface of CNTs, and this leads to a good electrical contact between the CNTs and metal oxide nanoparticles [7]. The defects created can thus act as reactive sites for the grafting of functional groups [8], [9]. Metal or metal oxide nanoclusters can be employed to decorate carbon nanotube sidewalls. Since metal or metal oxide nanoclusters show a wide range of physico-chemical properties (e.g. high catalytic activity, adsorption capacity, efficient charge transfer, etc.), they can provide a full range of reactivity towards different gases [10], [11].

The decoration of the surface of CNTs with metals, metal oxides or semiconducting nanoparticles improves the performance of CNTs [12] as well as enhancing their optical, electric, and magnetic properties [13], [14], [15]. Reports have indicated that the detection of toxic gases at high temperature can be improved by dispersing metal or semiconducting oxides onto CNTs. CNTs have been functionalized with Pd, Pt, Rh, and Au metals for CO, H₂, H₂S, NH₃, and NO₂ gas detection [16].

CNTs reactivity can be improved by functionalising their sidewalls with chemical groups [17], the defects created act as reactive sites for grafting functional groups [18], alternatively metal oxide nanoclusters can also be employed to decorate the side walls of the CNTs. Metal oxides or metal sulphides nanoclusters show a wide range of physico-chemical properties (e.g. high catalytic

activity, adsorption capacity, efficient charge transfer, etc.) which can provide a full range of reactivity towards different gases. In a way nanoclusters play a principal role in the gas detection pathway in which sensitivity and selectivity can be tuned based on the reactivity of the nanoclusters surfaces and on the nature of the charge transfer between the CNTs and the nanoclusters induced by gas adsorption [19], [20].

The study explores the dual roles played by nitrogen doping on CNTs and there gas detection characteristics on the embedded metals oxides and sulphides (SnO_2 , CuO and CdS) on these carbon nanomaterials.

4.1.1 Properties and synthesis of (N-CNTs decorated with metal oxide nanostructures for sensor applications)

Tin dioxide, SnO_2 , is an environmentally friendly semiconductor with a room temperature band gap of 3.6 eV. A lot of research interest to this material is attributed to the unique opto-electrical properties that have seen it being used as the anode material in lithium-ion batteries [21], [22], [23] and as an active layer in gas sensors [24], [25], [26]. CH_4 , CO , NH_3 and NO_2 constitute gases that have exhibited sensor response in SnO_2 decorated MWCNTs nanoparticles operated from room temperature to 250 °C [27].

Several methods have been used to synthesize nanostructured material, such as thermal evaporation [28], [29], chemical vapour deposition [30], the sol–gel technique [31], [32], [33] and the sonochemical route [34]. In addition the chemical-solution route [35]; [36] and chemical vapour phase method [37] have been explored in the deposition of SnO_2 nanoparticles on CNTs for enhanced performance as a composite based sensor.

4.1.2 N-CNTs decorated CdS for photovoltaic applications

The surface functionalization of CNT's allows the formation of novel 1-D hybrid materials. Recently, semiconductor nanoparticles have been found to exhibit a versatile range of potential applications, because of their unique size-tunable physical and chemical properties. They also represent ideal building blocks for constructing hybrid nanomaterial systems [38]. Accordingly, the organization of semiconductor nanoparticles on CNT's may produce novel nanocomposites that combine the properties of two functional nanoscale materials. The decoration of CNT's with organic/inorganic compounds through covalent and non-covalent bonds can give them new

properties and potentials for various new applications [39]. Decoration of multi-walled carbon nanotubes (MWCNT's) with *in situ* synthesis of CdS nanoparticles have been reported several years ago by Shi et al. and Liu et al. [40], [41]. Several synthesis methods have been employed to decorate the surface of CNT with CdS. The simplest one is through chemical solution route employed by several authors [40], [42], [43], [44], [39], [45], [46], [47], [48]. Hybridizing semiconductor nanoparticles on CNT surfaces can modify their optical and luminescent properties significantly and offer immense application potential in photo-electrochemical cells [49], [50], [51] as tunable light-emitting diodes [52], [53], [54] [55].

4.2 Results and Discussion

In this chapter, the characterization of metal oxide decorated on N-doped CNT is presented with key emphasis on their applications for gas sensing. As such the morphology, thermal and structural stability is examined after incorporation on CNT template. In addition the properties of the CdS decorated CNTs nanostructures are investigated for application in hybrid solar cells.

4.2.1 Transmission electron microscopy (TEM) analysis

Transmission Electron Microscopy has detected the morphological changes on N-CNT upon decoration of their tubular structure with metals based binary compounds.

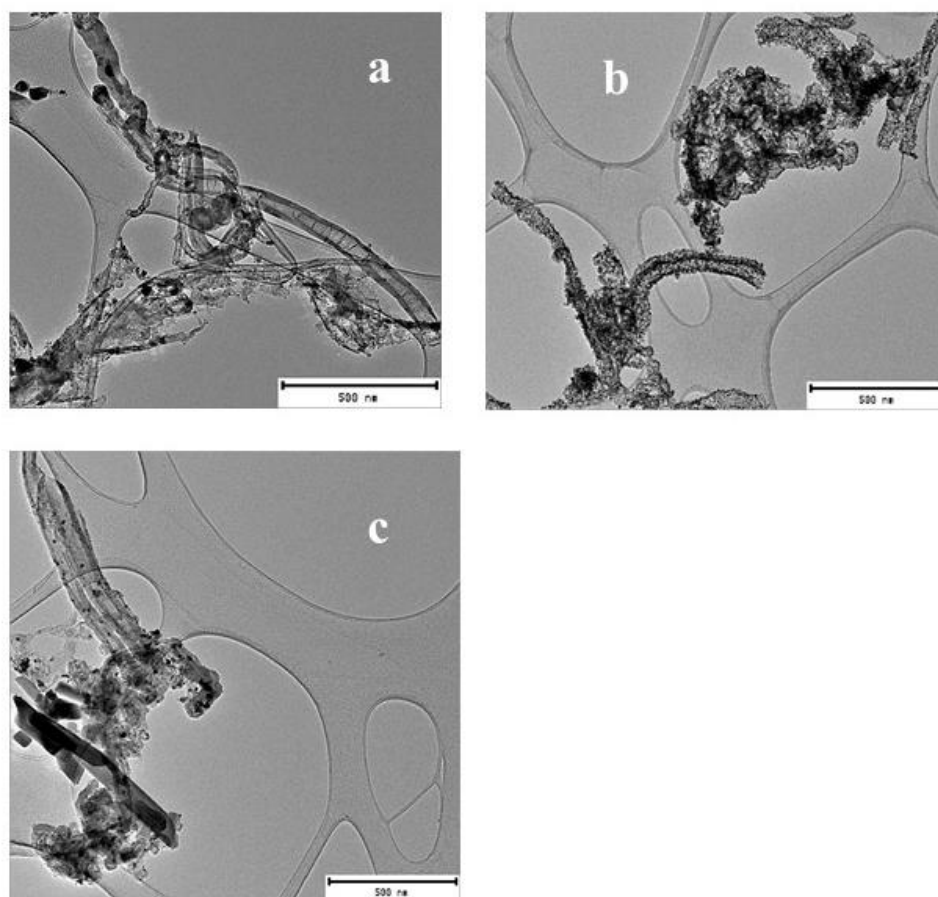
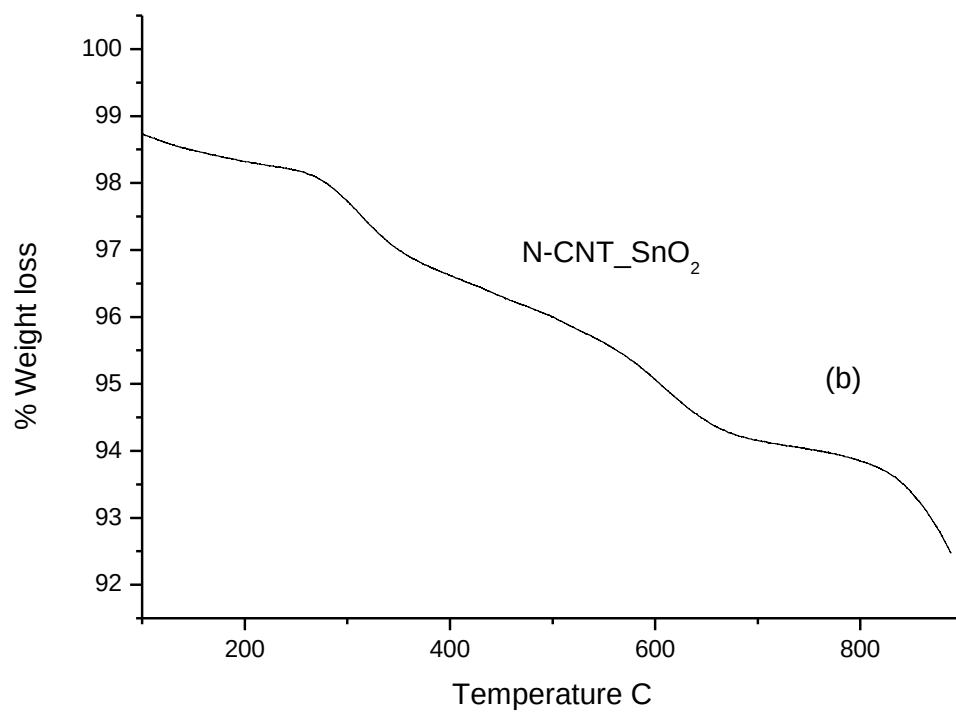
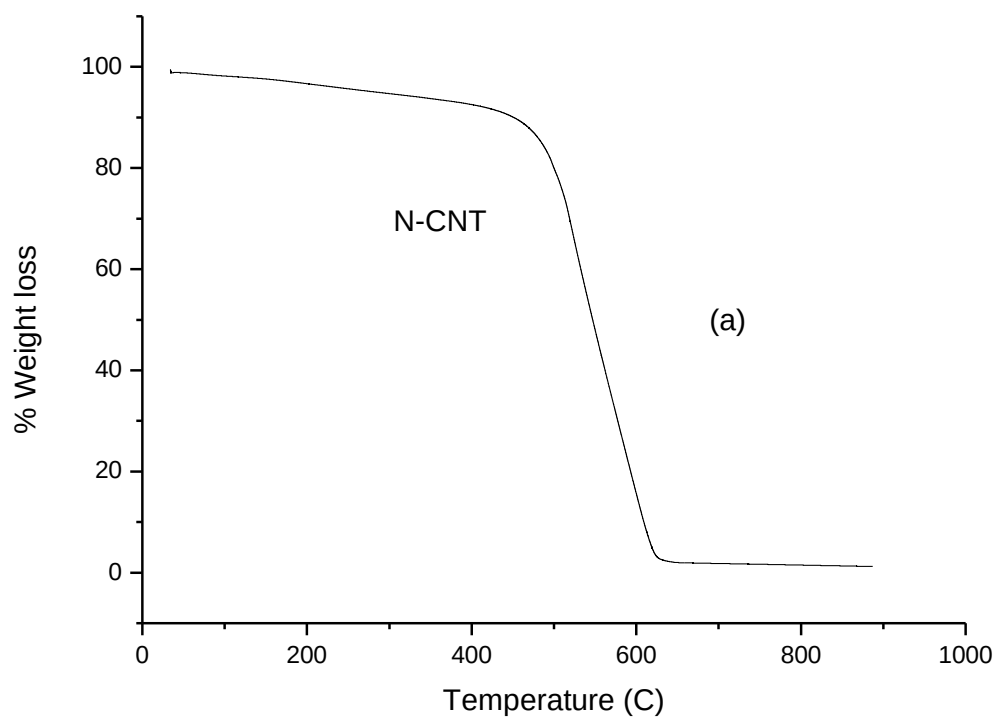


Figure 4-1: TEM images of (a) N-CNT, (b) N-CNT_SnO₂ and (c) N-CNT_CuO under a magnification of 500 nm.

Figure 4.1 (a) and (b) show the TEM images of N-CNT and N-CNT_SnO₂ nanoparticles taken at 500 nm magnification. The TEM image for the N-CNT clearly shows a bamboo-like morphology inside the structure of the tubes (Figure 4.1(a)). The presence of some concentric structures in Figure 4.1 (b) further confirms that SnO₂ particles have been attached at the surface of the tubes. The observed nanoparticles and amorphous carbon could be due to the opened tips of the tubes that were opened by the nitric acid during the purification process. Observation from the TEM images correlate with particle sizes derived from the XRD pattern of N-CNT_SnO₂ (provided in the next section).

Figure 4.1 (c) shows the TEM images of N-CNT_CuO nanoparticles. CuO are observed to be attached to the surface of the tubes. Observation from the TEM images correlate with particle size derived from the XRD pattern of N-CNT_SnO₂ as provided in the subsequent sections

4.2.2 Thermogravimetric (TGA) analysis of decorated N-CNT



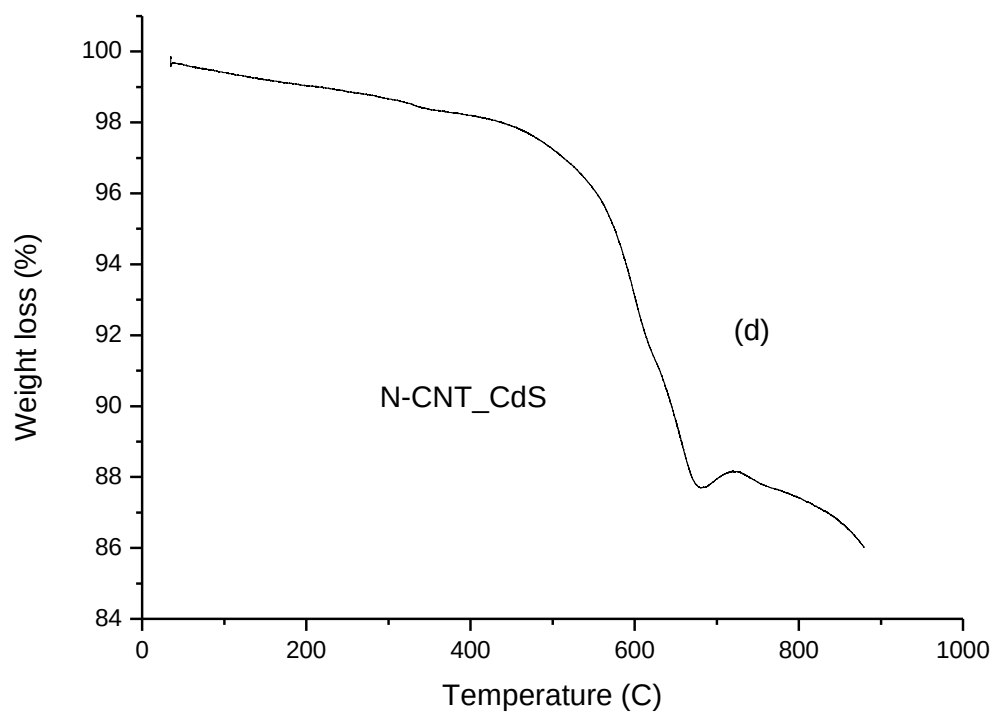
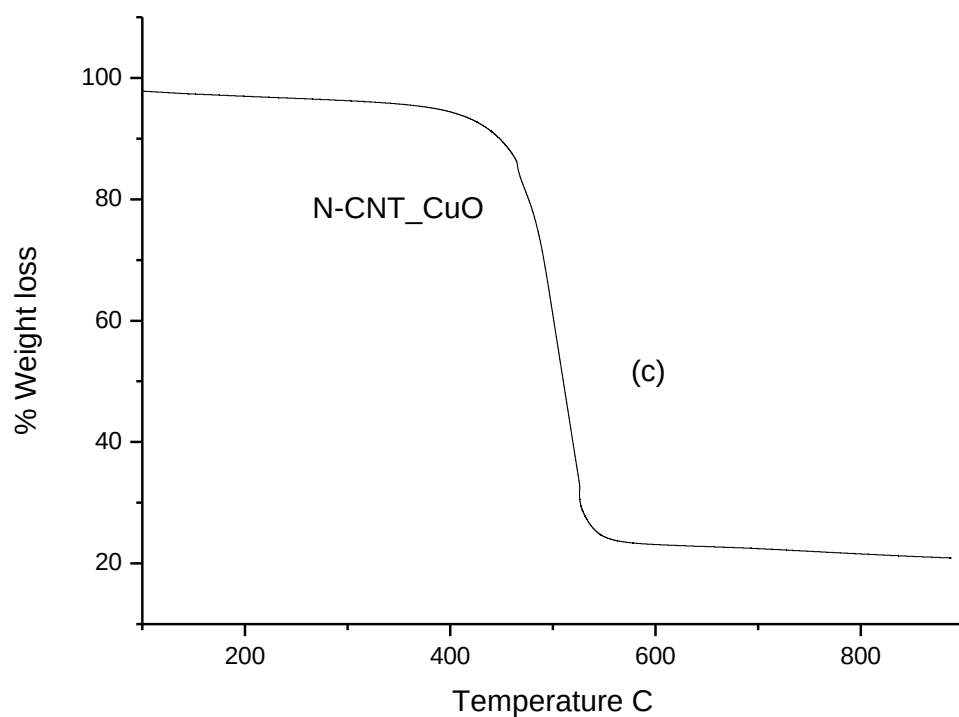


Figure 4-2: TGA profiles of (a) N-CNT, (b) N-CNT_SnO₂, (c) N-CNT_CuO and (d) N-CNT_CdS.

The Thermal Gravimetric Analysis measurements (TGA) plots for all the loaded samples are shown in Figure 4.2. Thermo-oxidative behaviour of N-CNT (Figure 4.2 (a)) shows one step decomposition and weight loss start at about 450 °C; whereas the weight loss in the loaded N-CNTs occur at a lower temperature. After purification (resulting in OH⁻ and C=O groups being attached) there was about 3% of impurities remaining within N-CNT. The purification process was to remove the support (Fe-Co/CaCO₃). The continuous weight loss of N-CNT_SnO₂ (Figure 4.2 (b)) is mainly due to desorption of water from the surface of the sample. The slow and steady weight change is as result of the loss of OH⁻ attached to the N-CNT followed by crystallization of SnO₂ (T_M = 1625 °C). Total weight loss of about 6.2% occurs between 97 and 886 °C in 3 steps.

In order to determine the content of CuO nanoparticles in the decorated N-CNT, TGA was carried out. The TGA analysis results are shown in Figure 4.2(c). The combustion of N-CNT began around 450 °C and was complete around 639 °C. The decomposition of N-CNT_CuO starts at about 420 °C and completes at 553 °C. When the N-CNT were coated with CuO about 70% weight loss arising from the decomposition of N-CNT could be observed at about 420 °C. The content of CuO embedded on N-CNT was estimated to be about 23% by weight. This is also confirmed by the TEM images of CuO decorated N-CNT.

The content of CdS nanoparticles in the decorated N-CNT was evaluated from the TGA patterns of Figure 4.2 (d). The TGA of N-CNT_CdS shows two 2 steps decomposition, one starting at about 40 °C and the other one at about 725 °C. Total weight loss of about 13.6% by weight which represent the embedded CdS nanoparticles on the surface of N-CNT. This is further supported by the high cohesive energies of the CdS nanoparticles, (T_M = 1750°C)

4.2.3 X-ray diffraction (XRD) analysis

The XRD pattern of N-CNT shown in Figure 4.3 typically has two carbon peaks namely the (002) and (100) reflections situated at about 30.7° and 52.8° respectively. The introduction of SnO₂ nanoparticles on the N-CNT leads to the formation of extra peaks as shown in Figure 4.3. The peaks for N-CNT coated SnO₂ nanoparticles are as reported in the literature [56], [57], [58], [59], [60], [61]. There are three main broad peaks for N-CNT_SnO₂ at 2θ 31.0°, 39.4° and 61.0°, corresponding to (110), (101) and (004) respectively. The peak positions (110) and (004) has

shifted with the introduction of SnO₂. Both N-CNT and N-CNT_SnO₂ show the diffraction peak to C (002). The diffraction peak corresponding of C (100) in N-CNT is heavily suppressed in SnO₂ coated N-CNT. The peak C (002) for N-CNT overlapped with the main peak assigned to SnO₂ (101). Additional diffraction peaks are also observed at 2 θ : 44.5°, 64.6°, 68.8°, 73.6°, 77.5° and 85.3° indicated as # in Figure 4.3 (Joint Committee on Powder Diffraction Standards [JCPDS Card No.: 00-041-1445]).

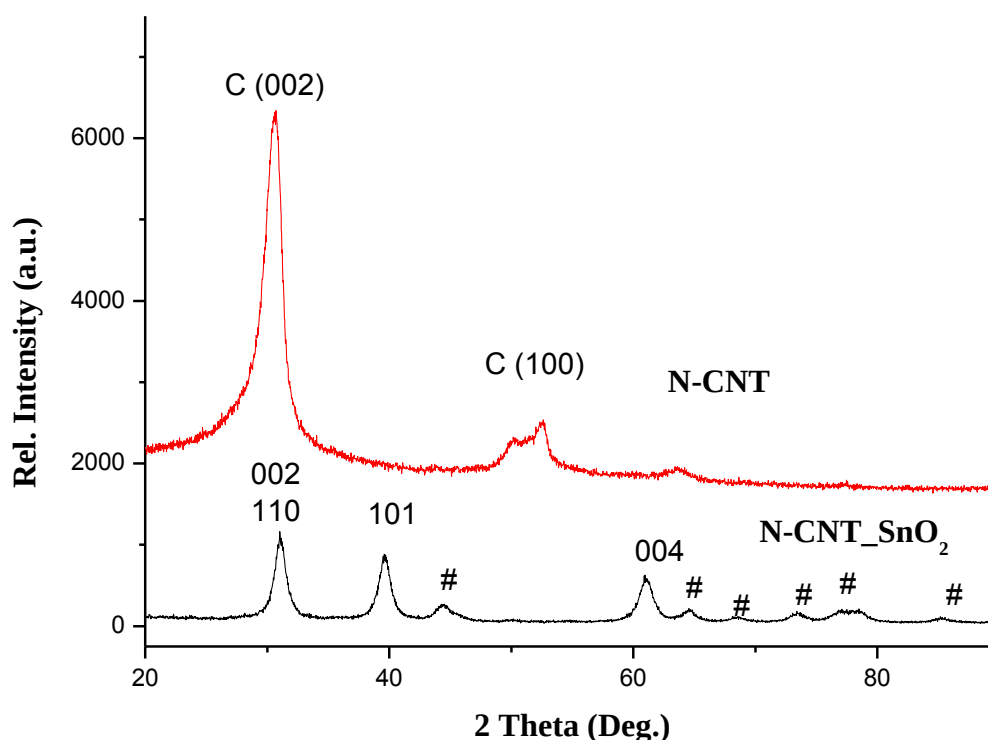


Figure 4-3: XRD spectra of (a) N-CNT and (b) N-CNT coated SnO₂ (N-CNT_SnO₂).

The peaks of N-CNT remains unchanged even after the calcination process, indicating that the graphitic structure of N-CNT is intact. The average particle size of the nanoparticle was confirmed using Debye-Scherrer equation; $d = \frac{K\lambda}{\beta \cos \theta}$ to be 6 nm for N-CNT and 10 nm for N-CNT_SnO₂, respectively.

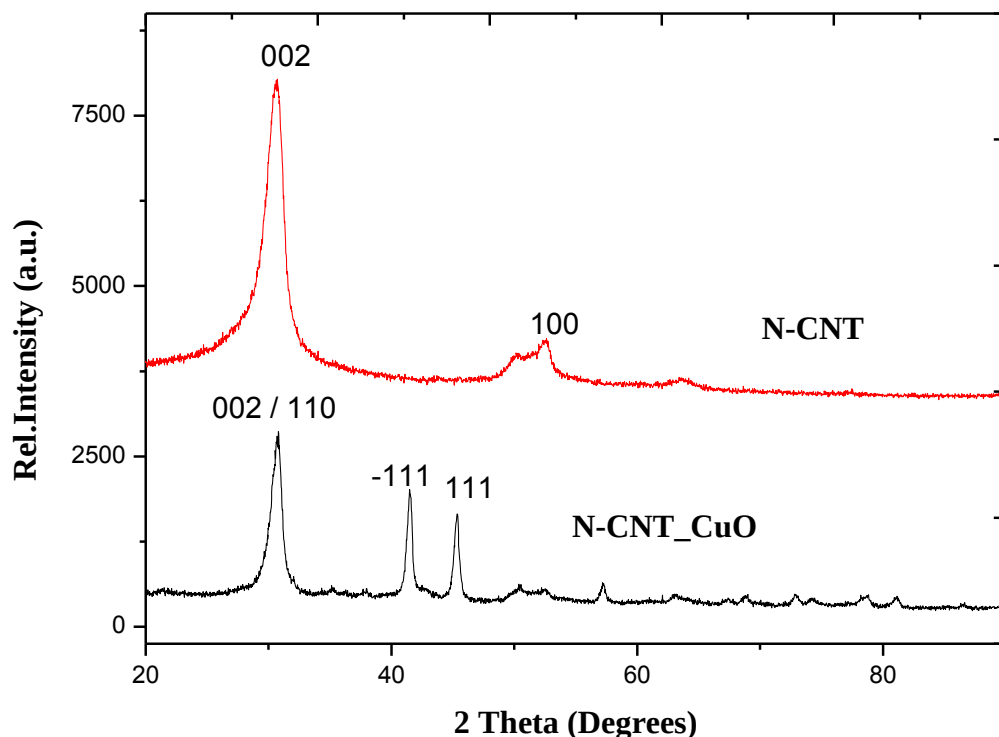


Figure 4-4: XRD spectra of N-CNT and N-CNT coated CuO (N-CNT_CuO).

The XRD pattern of N-CNT and N-CNT_CuO are shown in Figure 4.4. The peaks for N-CNT coated CuO nanoparticles corroborated those reported in the literature [62]. The diffraction peaks at $2\theta = 30.8^\circ$ and 52.8° are assigned to (002) and (100) reflections of the graphitic structure of CNTs. There are three main peaks for CN_x_CuO at $2\theta = 30.8^\circ$, 41.5° and 45.3° , corresponding to (110), (-111) and (111), respectively. Both N-CNT and N-CNT_CuO show peak of C (002). The diffraction peak corresponding of C (100) is present in N-CNT but is very weak in the CuO coated N-CNT. The peak C (002) for N-CNT overlapped with the main peak assigned to CuO (110). Additional diffraction peaks are also observed for N-CNT_CuO but they are very weak in intensity (all but one are for CuO (JCPDS Card No.: 01-073-6023)). The peaks of N-CNT remains unchanged even after the calcination process, indicating that the graphitic structure of N-CNT is intact. The average particle size of the nanoparticle was confirmed using Scherrer equation: $d = \frac{K\lambda}{\beta \cos\theta}$, where d is the mean crystalline particle size diameter, K is a constant (0.9), λ is the wavelength of the incident beam ($1.7902 \text{ \AA}$), β is the full-width half-maximum and θ is Bragg reflecting angle. The average crystallite size diameter estimated using Scherrer equation was 6 nm for N-CNT and 9 nm for N-CNT_CuO respectively.

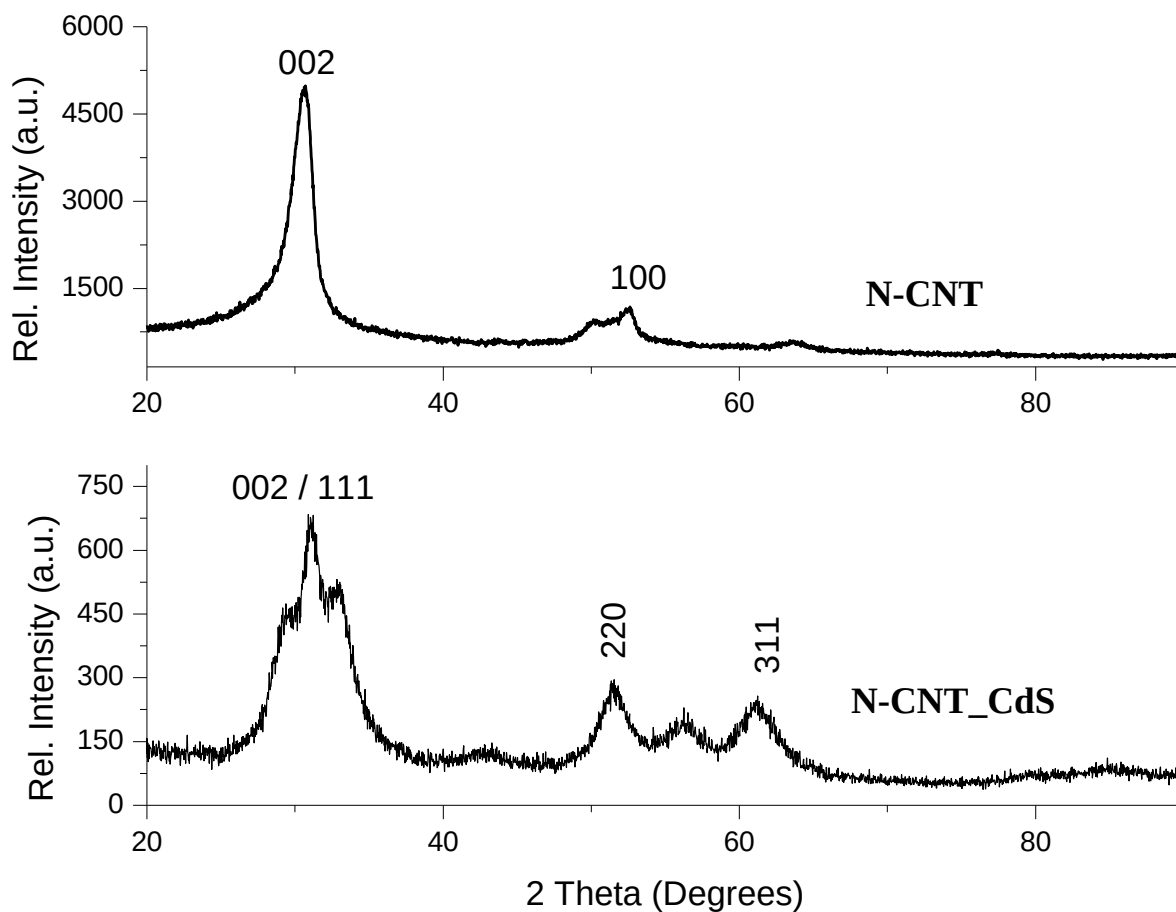


Figure 4-5: XRD patterns of N-CNT and N-CNT_CdS.

The XRD pattern of N-CNT and N-CNT_CdS are shown in Figure 4.5. The diffraction peaks for N-CNT coated CdS nanoparticles are assigned to the (111), (220) and (311) as reported in literatures [63] (JCPDS Card No.: 00-041-1049). The peak C (002) for N-CNT overlapped with the main peak assigned to CdS (111) for the CdS decorated N-CNT. The average particle size of the nanoparticle was confirmed using Scherrer equation. The average crystallite diameter estimated from the XRD spectra using Scherrer equation are 6 nm for N-CNT and 2 nm for N-CNT_CdS respectively.

4.2.4 Raman spectroscopy

Optical characterization (Raman and FTIR) provides information on the nature of Raman active defects and the changes in the vibrational properties after loading doped CNTs with metallic based binary compounds. The effect of loading of doped N-CNT is presented by monitoring the D and G vibration modes of CNT as shown in the Raman spectra of Figures 4.6 – 4.8 and summarised in Table 4.1.

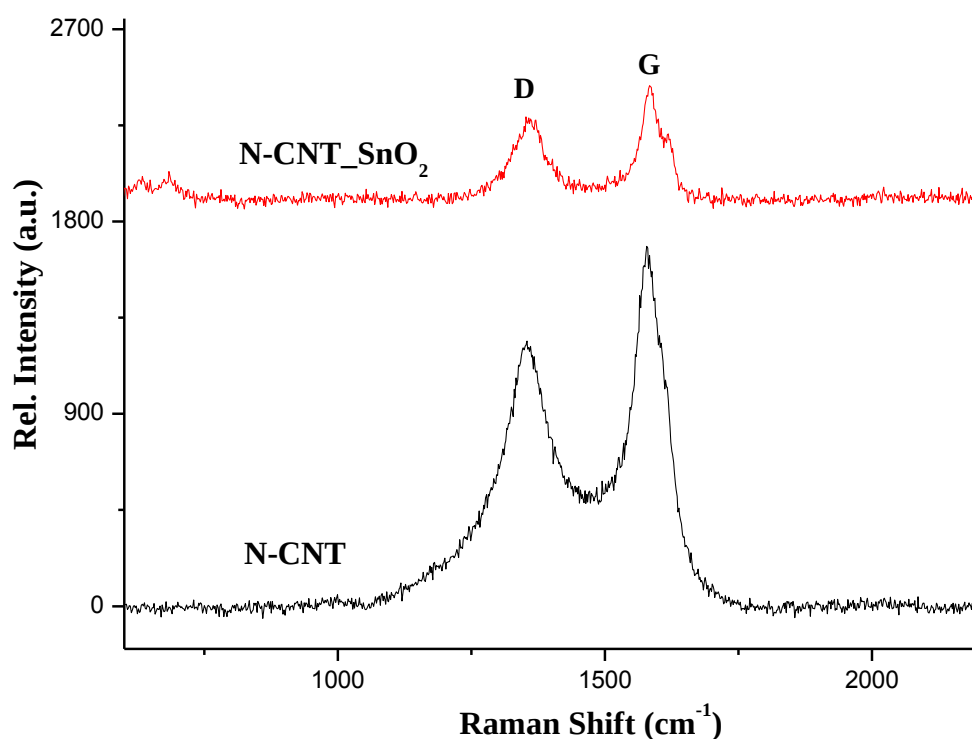


Figure 4-6: Raman spectra of N-CNT and (b) N-CNT_{SnO₂}.

Table 4-1: D-band, G-band and I_D/I_G ratios of N-CNT, N-CNT_{SnO₂}, N-CNT_{CuO} and N-CNT_{CdS}

Sample	D-band (cm ⁻¹)	G-band (cm ⁻¹)	I_D/I_G
N-CNT	1363	1582	0.68
N-CNT _{SnO₂}	1355	1586	0.76
N-CNT _{CuO}	1360	1584	0.63

N-CNT_CdS	1403	1546	0.88
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The Raman spectra of N-CNT and N-CNT_SnO₂ shown in Figure 4.6 have two strong peaks which correspond to the D (amorphous carbon) and G (graphitic carbon) bands typical for MWCNTs respectively. The D-band is due to the presence of defects, disorder and sp³-hybridized carbon atoms present in the sample while the G-band is ascribed to the presence of sp²-hybridized carbon atoms [64]. The D-band and G-band peak positions and their corresponding I_D/I_G ratios for N-CNT and N-CNT_SnO₂ are summarized in table 4.1. In the SnO₂ decorated sample, a shift in both the D-band and G-band compared to the purified sample (N-CNT) is observed. This can be due to the interaction between the nanoparticle and N-CNT. This is also confirmed from the higher I_D/I_G ratio of N-CNT_SnO₂ shown in Table 4.1.

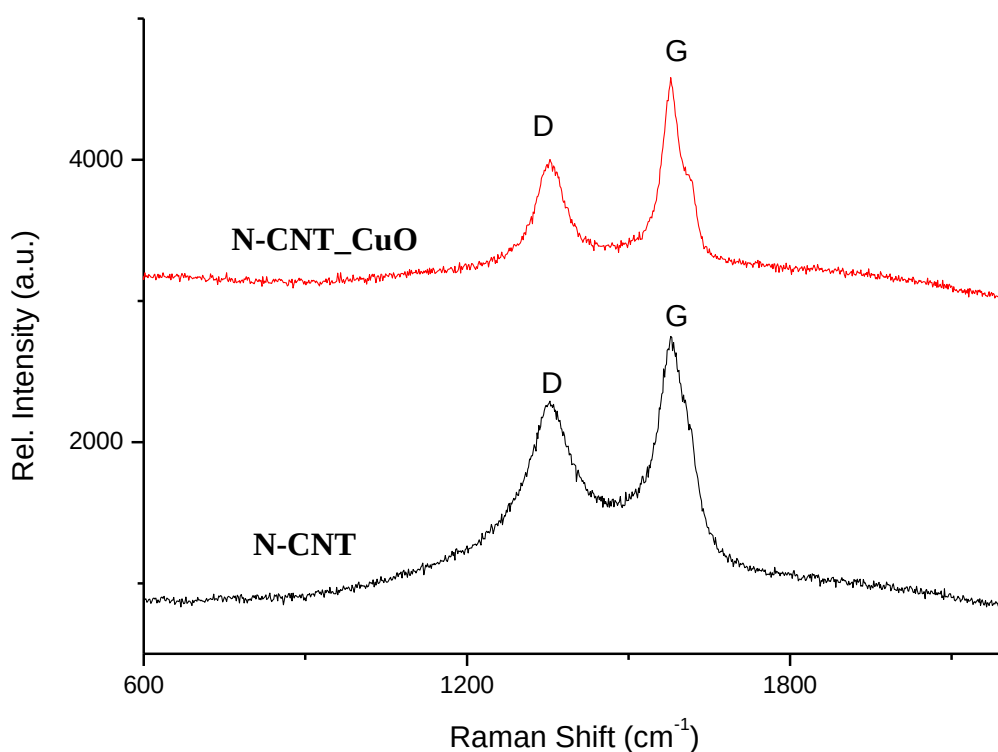


Figure 4-7: Raman spectra of N-CNT and N-CNT coated CuO (N-CNT_CuO).

Both the Raman spectra for N-CNT and CuO decorated N-CNT in Figure 4.7 show two strong peaks which correspond to the D (Amorphous carbon) and G (Graphitic carbon) bands ascribed to MWCNTs. The D-band is due to the presence of defects, disorder and sp³-hybridized carbon atoms present in the sample and the G-band is due to the sp²-hybridized carbon atoms [64]. The

D-band and G-band peak positions and their corresponding I_D/I_G ratios for N-CNT and N-CNT_CuO are given in Table 4.1. In the case of the CuO decorated sample there is no shift in both the D-band and G-band compared to the purified sample (N-CNT). This can be due to the fact that the interaction between the CuO nanoparticle and N-CNT is very small, this is also confirmed from the lower value of I_D/I_G ratio of N-CNT_CuO shown in Table 4.1.

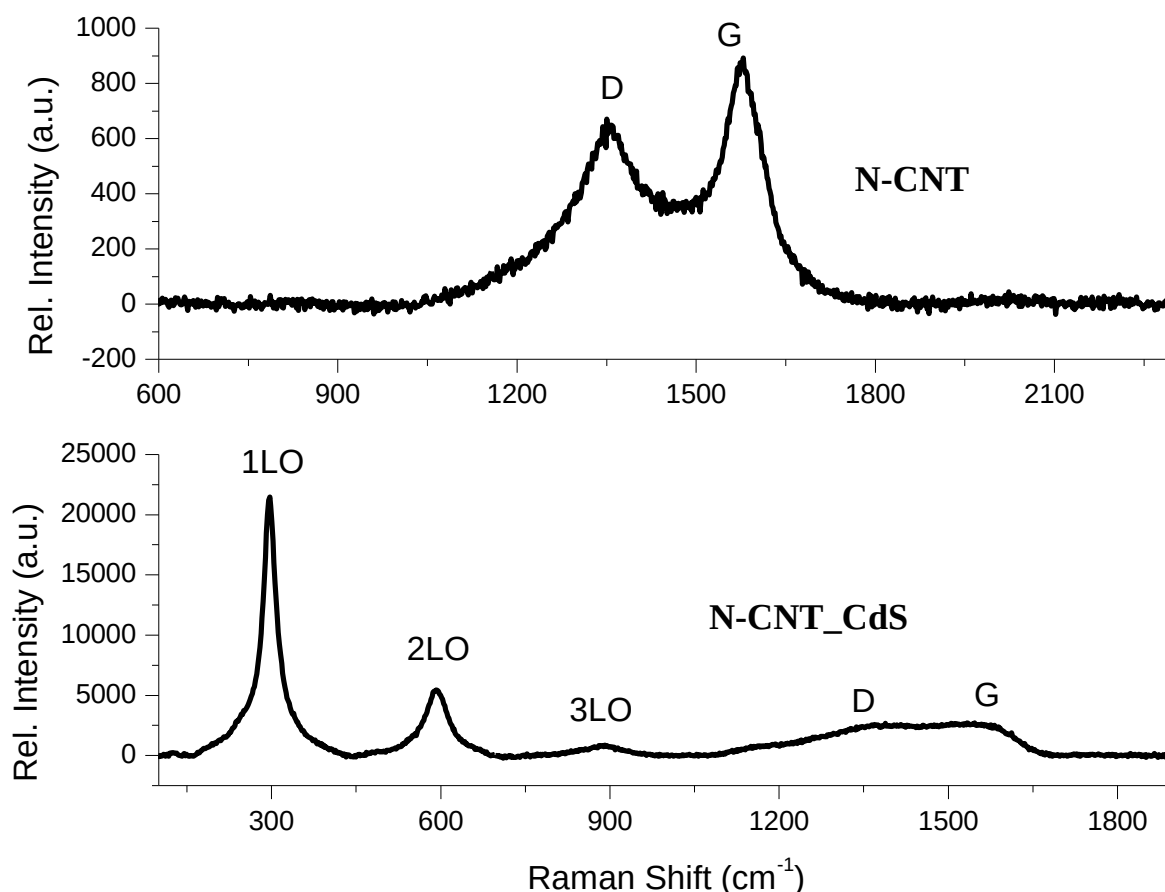


Figure 4-8: Raman spectra of N-CNT and N-CNT_CdS.

Figure 4.8 shows the Raman spectra of N-CNT and N-CNT loaded CdS. The Raman spectrum of N-CNT shows two strong peaks centred at 1350 and 1572 cm^{-1} , which correspond to the D (Amorphous carbon) and G (Graphitic carbon) bands typical for MWCNTs respectively. The spectrum for N-CNT_CdS shows 3 additional bands located at 293 , 589 and 885 cm^{-1} corresponding to the first-order longitudinal-optical (1LO) phonons, the second-order longitudinal-optical (2LO) and third-order longitudinal-optical (3LO) respectively. These three bands belong to CdS nanoparticles. There are also two weak bands belonging to MWCNTs

corresponding to the D and G bands, located at 1366 and 1585 cm^{-1} respectively [65], [66]. There is a shift of the D- and G- bands positions in N-CNT_CdS to higher and lower wavenumbers respectively. This could be due to the presence of the CdS particles on the surface of N-CNT giving rise to the presence of three extra peaks assigned to 1LO, 2LO and 3LO [66] resulting into more defects which is confirmed from the higher value of I_D/I_G ratio of N-CNT_CdS shown in Table 4.1.

4.2.5 Fourier transform infrared (FTIR) analysis

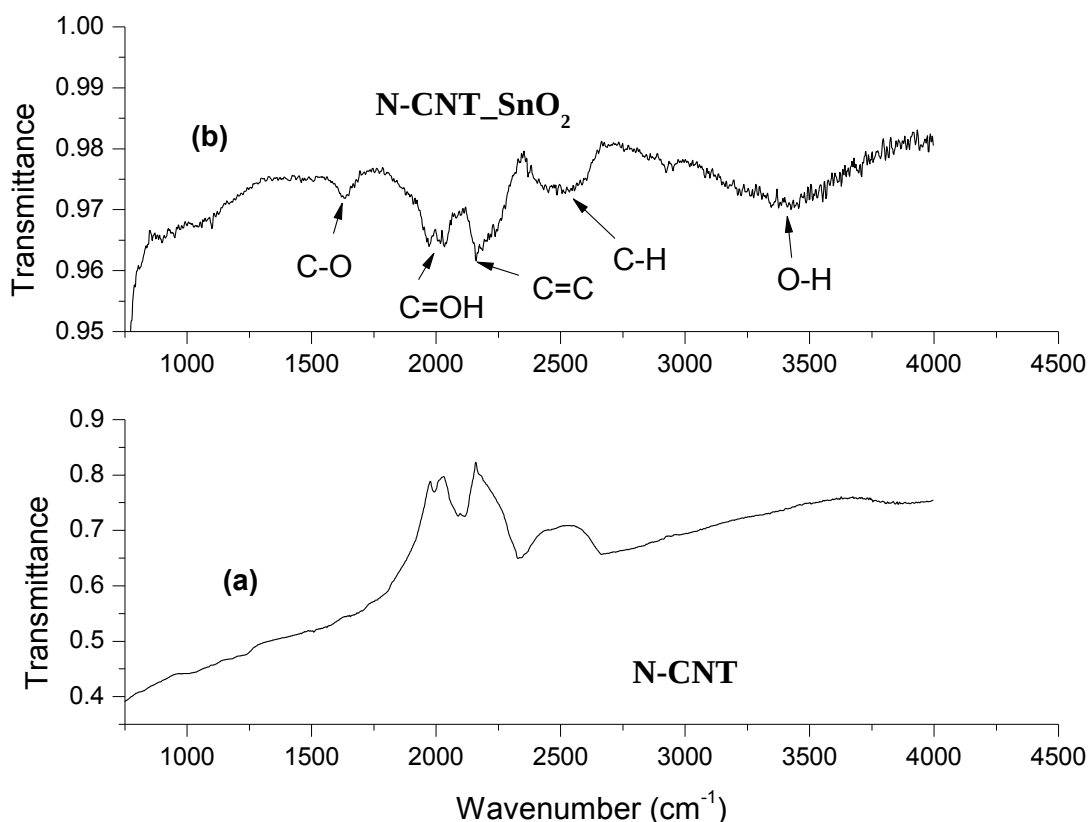


Figure 4-9: FTIR spectra of (a) N-CNT and (b) N-CNT_SnO₂

The FTIR spectra can be used to detect functional group on the N-CNT surface during the purification process. In the FTIR spectra of N-CNT (Figure 4.9), the C=C stretching vibration is observed [67]. The C=O stretching vibration indicates the presence of carboxylic groups created during functionalization of N-CNT [68] and O-H stretching vibration originating from absorbed water molecules on the amorphous carbon present in N-doped MWCNTs. The O-H functional

group is formed in the chemical treatment during the purification process [69]. These functional groups at the surface of N-CNT imparts a hydrophilic nature to the nanotubes and also acts as good anchoring sites for the deposition of oxide nanoparticles. The FTIR spectra of N-CNT_SnO₂ shown in Fig 4.9 confirm the presence of these functional groups.

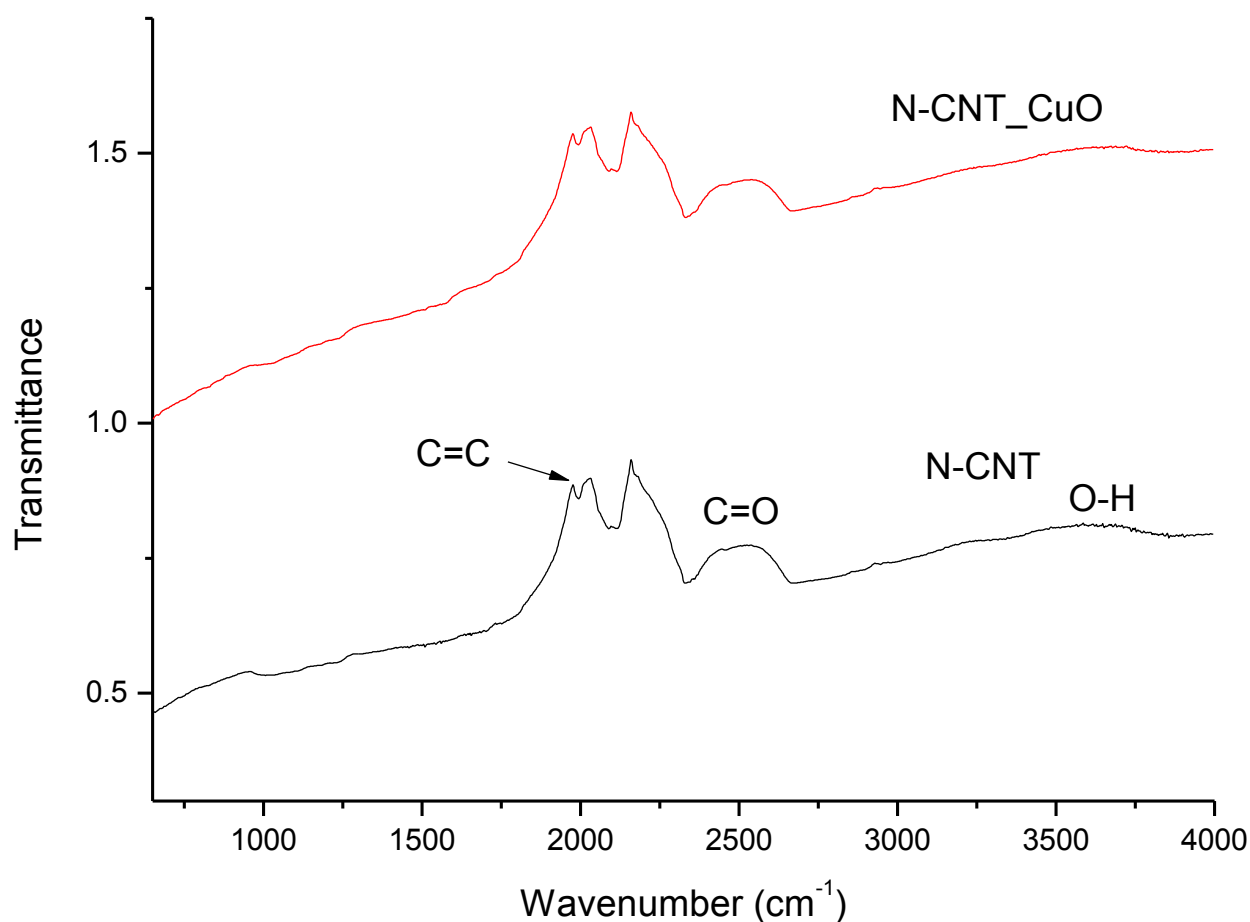


Figure 4-10: FTIR of N-CNT and N-CNT_CuO

In the FTIR spectra of N-CNT shown in Figure 4.10, the peak C=C stretching vibration is due to the structure of CNTs [67] the C=O stretching vibration indicates the presence of carboxylic groups created during functionalization of N-CNT [68] and O-H stretching vibration originating from absorbed water molecules on the amorphous carbon present in N-doped MWCNTs [70]. The FTIR spectra of N-CNT_CuO confirms these functional groups as well (Figure 10). These functional groups at the surface of the nanotubes acts as good anchoring sites for the deposition of oxide nanoparticles. The spectra of N-CNT_CuO confirm the presence of C=C, C=O and O-H functional groups.

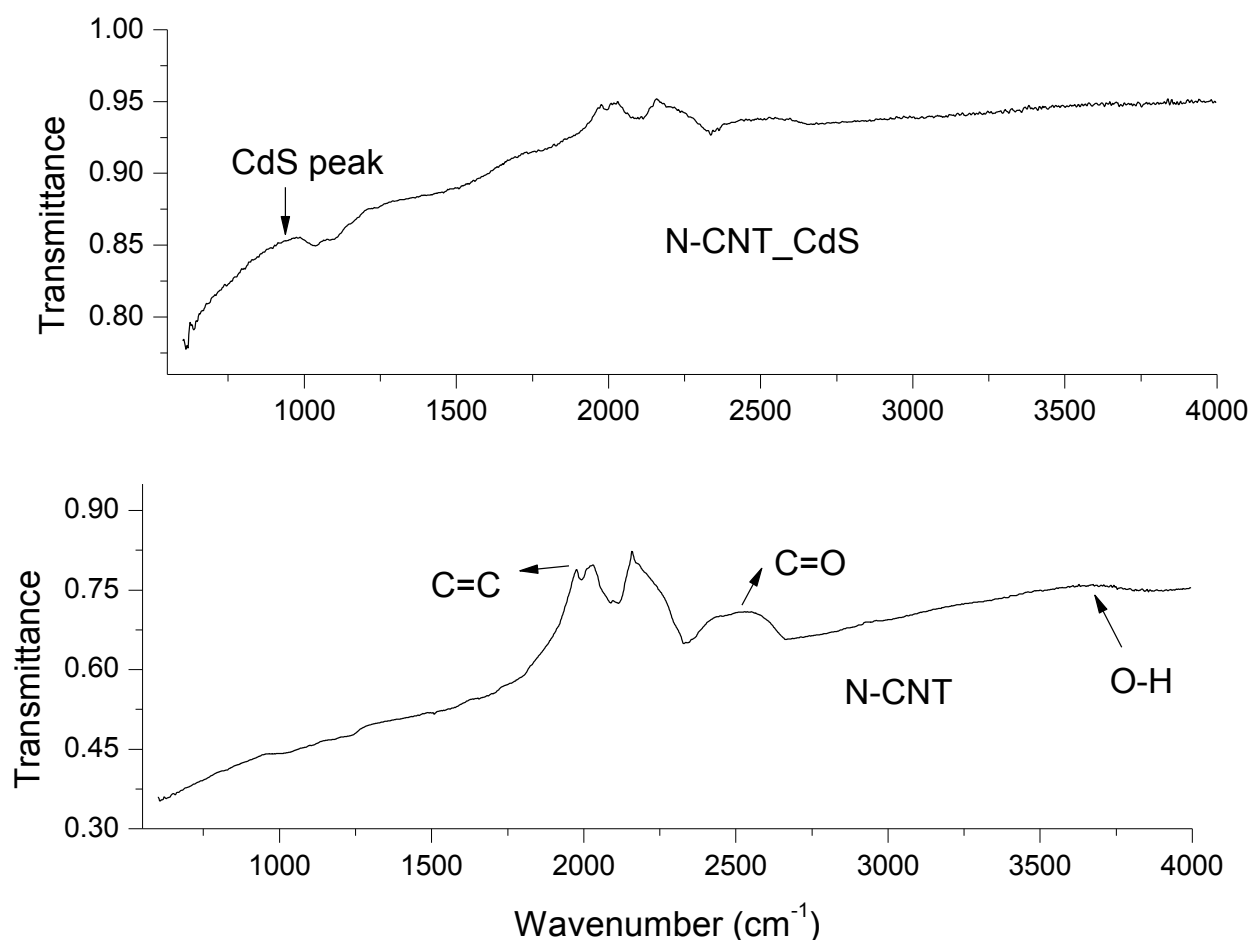


Figure 4-11: FTIR spectra of N-CNT and N-CNT_CdS.

The FTIR spectrum of N-CNT_CdS is shown in Figure 4.11. In the FTIR spectrum of N-CNT, the peak C=C stretching vibration is due to the structure of CNTs [67] the C=O stretching vibration indicates the presence of carboxylic groups created during functionalization of N-CNT [68] and O-H stretching vibration originating from absorbed water molecules on the amorphous carbon present in N-doped MWCNTs [71], [72], [73]. The spectra of N-CNT_CdS compare to that of N-CNT except that there is an additional peak belonging to CdS (see Fig.4.12). The peaks belonging to C=O and O-H becomes weak in N-CNT_CdS structure indicating that the CdS deposition was successful on the surface of N-CNT. This acts as sites for anchoring the CdS nanoparticles.

4.3 Conclusion

SnO₂ and CuO nanoparticles were successfully incorporated/encrusted on N-CNT by wet chemical method. The TEM images have revealed a uniform coverage of SnO₂ and CuO nanoparticles on

the surface of N-CNT with a surface thickness variation in the range 20nm. The samples are thermally stable after decoration. From the Raman spectra, a shift of the D and G bands with the incorporation of the nanoparticles in all the samples but N-CNT_CuO is observed, this is attributed to the increase in the strain of the carbon lattice. CdS nanoparticles were successfully deposited on the surface of N-CNT.

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Chapter 5: Characterization of aligned nitrogen-doped multi-walled carbon nanotubes

5.1 Introduction

Carbon nanotubes (CNTs) have attracted considerable attention for use in optoelectronic devices, as tethering templates for sensors, as well as being applied in field emission devices [1,2]. These diverse applications are driven by their unique combination of properties. Their high chemical stability, excellent mechanical strength, and the high thermal and electrical conductivity of CNTs has seen them explored for nanoelectronics, energy conversion and as supports for quantum dots [3]. Generally, most of these properties have been explored on pristine CNTs (multi-walled (MW) and single-walled (SW)). Despite the enormous application potential of pristine CNTs, the functionalization of the MWCNT lattice is bound to make inroads for novel applications by tuning their electrical, magnetic and optical properties. One of the approaches to modify the surface or internal structure of these materials is by nitrogen doping due to the presence of additional electrons in the conduction band [4]. This feasible strategy can therefore tune the electronic properties of CNTs to span between metallic and narrow gap semiconducting characteristics [5]. For instance, the vertical alignment of nitrogen doped MW-CNTs has been found to enhance their electro catalytic activity due to the presence of nitrogen thus enabling their potential exploration as nanoscale energy materials and sensors. Despite the enhancement of the electrical properties of CNTs by N-doping [6-8], the crystallinity and the integrity of the tubular structure of the CNTs can be severely compromised [9]. This is particularly problematic for large area synthesis which is pre-requisite for optoelectronic and sensor applications.

The synthesis of most CNTs is mediated by supported catalysts and often the catalyst is left embedded in the CNT. The location of the catalysts within the tube is random and without fine control which is an essential requirement for device fabrication. The purification of MW-CNTs to remove the catalyst and the amorphous carbon residues to ensure adequate characterization of the device properties is a necessary and sufficient condition for any device development. In addition, purification permits the functionalization of chemical groups on the surface of the carbon structure thereby enabling the tuning of their physico-chemical properties. Most of the catalysts used for CNT synthesis are magnetic in nature (such as Fe). These catalysts can be located on the surface or embedded in the CNTs depending on the concentration of the catalyst used in the synthesis.

Thus the CNTs as a result exhibit magnetic properties as a result of the Fe-nanoparticle residue embedded in the tubes after the purification process. For instance, Tsukagoshi et al. and Sahoo et al. reported that the inclusion of Fe (or Co) in the CNTs in a controlled manner to form heterostructures or superlattice layers within the tubes provided extensive implications and benefits in the field of spintronics [10], [11]. Magnetic sensors can be achieved with intentional dopant incorporation of ferromagnetic atoms. However, control of the impurities that remain embedded within the tubes pose a major challenge for the application of CNTs in magnetic, electronic, or/and related devices. [11]. To solve some of the problems associated with the metal nanoparticles, recent research reports have indicated that the structural orientation (vertically aligned or randomly) of CNTs can be an interesting area of study. For instance, aligned CNTs (A-CNT) are useful as sensors due to their large surface area [12]. Thus evaluating the magnetic properties of the N-doped vertically aligned MWCNTs containing residual impurities could be the keynote to finger print the purification process and as well as understand the role of nitrogen doping. In this study, nitrogen doping is used to limit the concentration, shape and aspect ratio of NPs embedded in the cavity of the carbon nanotubes through the formation of bamboo like structures. The magnetic properties of aligned N doped MWCNTs with fixed concentration of ferrocene catalyst have been subsequently investigated following purification cycles to eradicate the Ferromagnetic impurities on the surface of the aligned carbon nanotubes. The nature of the impurities is established using combination of hyperfine interaction techniques and a SQUID magnetometer.

5.2 Results and discussion

5.2.1 Purification of N-A-CNTx

The N-A-CNTs were purified with an acid solution to remove the residual Fe nanoparticles and to introduce oxygen functional groups on the surface. Purification was performed using 55% HNO₃ solution at 110 °C for 6 hours. The acid-treated carbon materials were then filtered and washed several times with distilled water until the pH of the filtrate was neutral. The nitrogen-containing materials were dried at 120 °C for 12 hours. Treatment with HNO₃ has been found to oxidize some of the Fe⁰ to Fe₂O₃, [16].

5.2.2 Morphology of N-A-CNT_x by SEM and TEM

The aligned N-A-CNTs were found to be closely packed in bundles or arrays as shown by the cross-section SEM images in Figure 5.1(a, c and e).

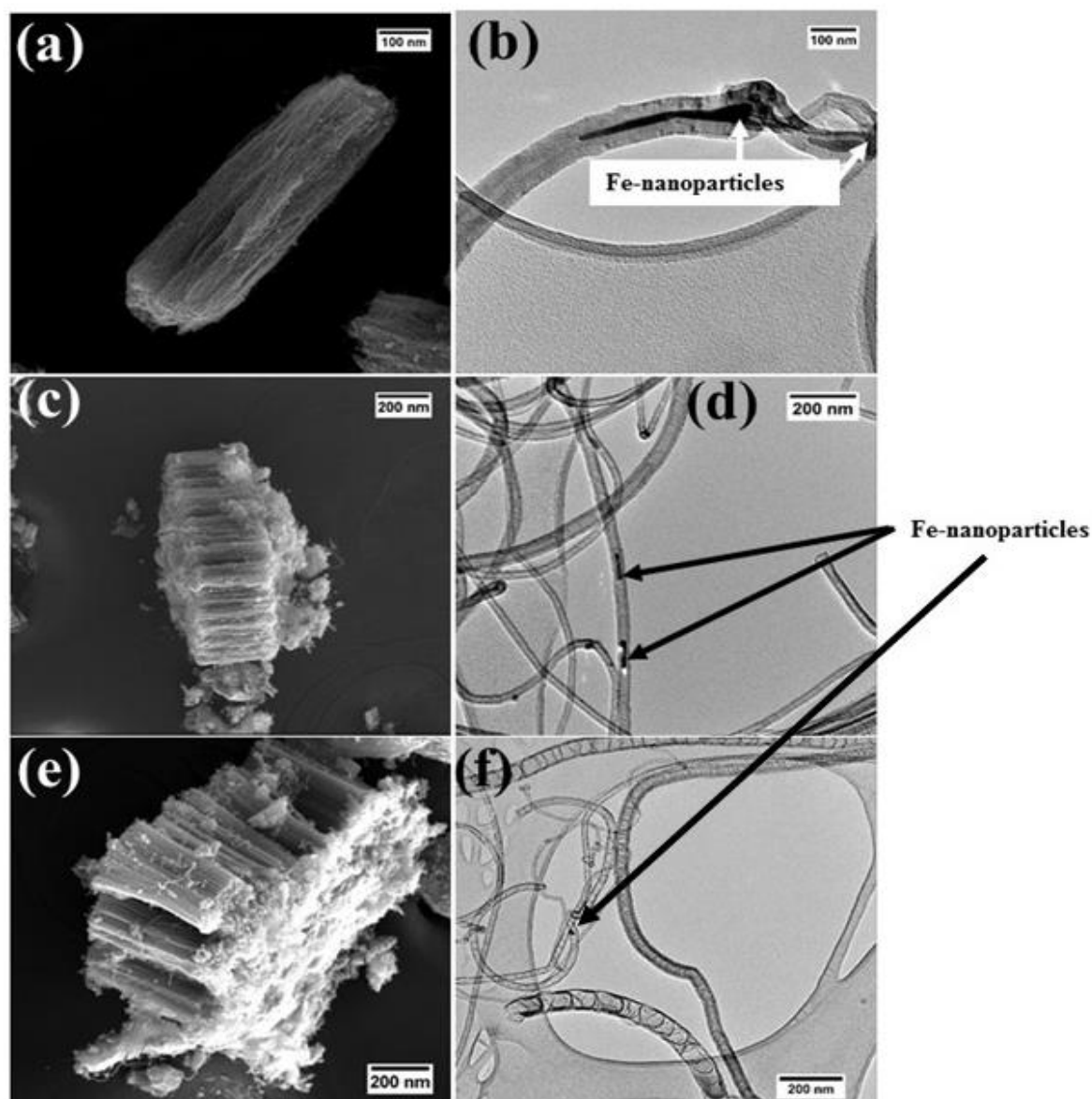


Figure 5-1: SEM (a, c and e) and TEM (b, d and f) images of N-A-CNT_x ($x = 0$), N-A-CNT_x ($x = 0.5$) and A-CNT_x ($x = 1$) after purification. A closer look at the Fig. 5.1 (f) it is clearly seen that there are Fe NP intercalated in the bamboo regions of the aligned carbon nanotubes.

The N-A-CNT_x length was determined to correspond to the bundle height; which was found to be 614 nm ($x = 0$), 286 nm ($x = 0.5$) and 425 nm ($x = 1$). Since all the experimental parameters were

the same, the decrease in length can be attributed to the formation of the bamboo structure due to the incorporation of N – atoms. Hao and co-workers [17] reported the decomposition of acetonitrile at high temperatures to a variety of CN radicals. Bulusheva and co-workers [18] performed quantum chemical calculations of N-CNT_x nanotubes and found that the nitrogen atom preferentially occupied a site in a pentagonal ring. The formation of such rings promoted the closure of the tube; thus leading to shortening of N-A-CNT_x in the presence of acetonitrile ($x = 0.5, 1$).

The TEM images of the purified samples are also shown in Figure 5.1(b, d and f). All the samples are multiwall nanotubes with a nearly cylindrical layer packing. The TEM images confirm the presence of Fe-nanoparticles embedded in the tubes. The nanoparticle sizes ranged from 22 to 450 nm. The TEM image for N-A-CNT ($x = 0$) illustrated a hollow structure with an average outer diameter of about 52 ± 11 nm however for N-A-CNT_x ($x = 0.5$ and 1) bamboo-like and corrugated structures were observed. This indicates the incorporation of nitrogen into the N-A-CNT_x. The average outer diameter for $x = 0.5$ and $x = 1$ were calculated to be 56 ± 39 and 85 ± 49 nm, respectively. It is noteworthy to mention that with the increase of nitrogen content the inner diameter increased while the outer diameter and the wall thickness decreased.

5.2.3 Thermal stability of N-A-CNT_x

Thermal Gravimetric Analysis (TGA) was used to evaluate the thermal stability of purified N-A-CNT_x and a summary of the results is presented in Table 5.1. The minima in the first order derivative of the TGA curves indicates the decomposition temperatures of N-A-CNT_x [19]. Interestingly, addition of nitrogen marginally decreases this value from 583 to 574 °C. This can be attributed to the formation of structural defects which are dependent on the configuration of nitrogen in the lattice of the CNT's structures [18–20]. The results are in agreement with recent research reports which indicated that an increase in nitrogen content resulted in the formation of less thermally stable N-CNTs due to the presence of more structural defects and disorder achieved by the introduction of reactive sites in the N-CNTs [20–23]. Finally, the residual masses of the catalyst impurities after the decomposition of carbon were estimated to be 5.2, 6.3 and $3.6 \pm \%$ for $x = 0$, $x = 0.5$ and $x = 1$, respectively.

Table 5-1: Residual mass and thermal stability temperatures of purified N-A-CNT_x.

Sample	Residue mass (%)	Thermal decomposition stability (°C)
x = 0	5.2	583
x = 0.5	6.3	577
x = 1.0	3.6	574

5.2.4 Vibrational properties of N-A-CNT_x by Raman spectroscopy

The effect of nitrogen incorporation on the structural properties of the N-A-CNTs were studied by single wavelength Raman spectroscopy [24], [25]. Figure 5.2 shows the first and second order harmonics of the D (defect mode) and G (graphite mode) bands. The intensity of the D-band is related to the presence of structural defects due to changes in the bonding configuration of the carbon atoms and other defects induced by nitrogen [26–30]. The G-band corresponds to the tangential vibrations of the graphitic carbon atoms in graphite [19].

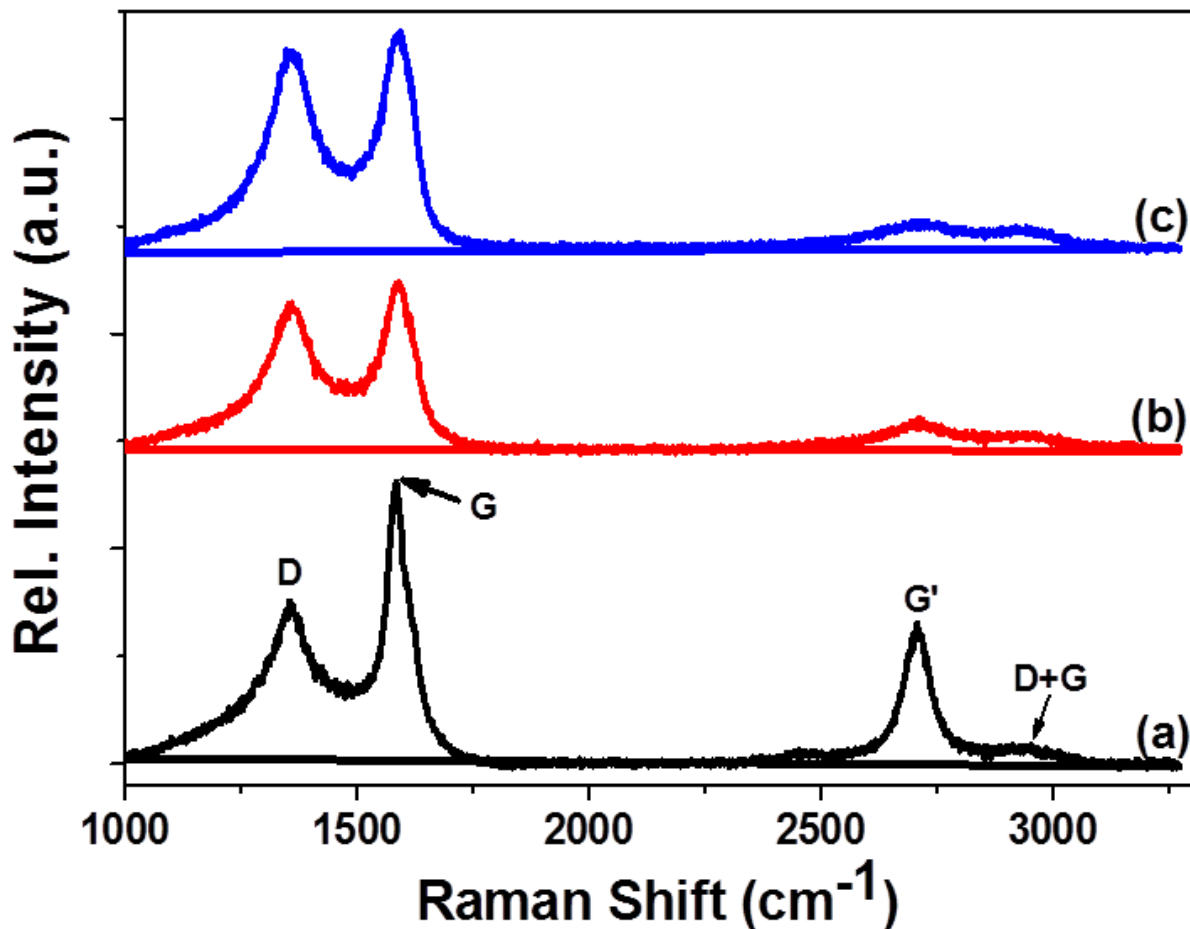


Figure 5-2: Raman spectra of N-A-CNT_x (a) ($x = 0$), (b) $x = 0.5$ and (c) $x = 1$.

A summary of the vibrational modes for N-A-CNT_x is presented in Table 5.2. The G' band at ca. 2700 cm⁻¹ is the second-order Raman peak which is attributed to a D band overtone (1356 cm⁻¹) [26, 27, 31]. The G' band corresponds to a two-phonon process and it is sensitive to the incorporation of nitrogen in CNTs. From the Raman spectra (Figure 5.2) it is evident that the increase in nitrogen content reduces the G' band intensity. The D, G and G' bands are narrowest when x = 0 indicating the better quality of the N-A-CNT that do not contain nitrogen. The G' band for the pristine N-A-CNT_x (x = 0) has the highest intensity. This indicates that this material only contains a few layers of graphene sheets with 3D structural defects in the lattice [33–35]. Addition of nitrogen suppresses the G' band and the D+G combination mode (2935 cm⁻¹) due to the induced structural disorder [36]. The quantity of structural disorder can also be determined from the intensity ratio of the D and G bands. Table 5.2 shows that this ratio increases with increasing nitrogen content, which indicates the enhancement of disorder in the CNT lattice. This disorder manifests itself as a result of nitrogen incorporation. Further indication of the disorder due to nitrogen addition is shown by the increase in the full width at half maximum (FWHM) and in the shift of the G' band.

Table 5-2: Raman spectral data for N-A-CNT_x (x = 0, 0.5 and 1).

A-CNT_x Sample	D band cm⁻¹	G band cm⁻¹	G' band cm⁻¹	D + G band cm⁻¹	I_D/I_G	G' FWHM	N (at %)
x = 0	1356	1587	2707	2942	0.55	69	0
x = 0.5	1358	1589	2748	2935	0.83	395	2.2
x = 1	1359	1587	2772	2935	0.89	604	3.8

5.2.5 X-ray photoelectron spectroscopy (XPS) studies on Nitrogen defects in N-A-CNT_x

The XPS was used to determine the content and relative ratio of different N-functional groups incorporated in the N-A-CNT_x. The elemental compositions of N-A-CNT_x is shown in Table 5.3 with the nitrogen content (N/C) for the samples x = 0.5 and x = 1 calculated to be 2.13% and 3.05% respectively.

Table 5-3: Elemental compositions of N-A-CNT_x.

Samples	C (at. %)	N (at. %)	O (at. %)	N/C
x = 0	90.73	-	9.27	-
x = 0.5	87.88	1.87	10.25	2.13
x = 1	84.78	2.59	12.63	3.05

Figure 5.3 shows the C1s (a, b and d) and N1s (c and e) spectra for x = 0, 0.5 and 1. The C1s spectra were deconvoluted into five components with the binding energies 283.9 – 284.0 eV (sp^2 carbon), 284.9 – 285.2 eV (sp^3 carbon), 285.8 – 286.3 eV (carbonyl groups), 287.8 – 288.1 eV (carboxyl groups) and 290.1 – 290.7 eV ($\pi - \pi^*$ satellite peak) [37–41]. The main peak of the C1s at 284.6 eV is due to sp^2 carbon atoms and is associated with the graphite structure of the carbon [42], [43]. The C1s spectra of N-A-CNT_x is shifted towards higher binding energies with nitrogen incorporation from 284.9 eV (x = 0) to 285.2 eV (x = 1) (Table not shown). As the content of nitrogen increases, the atomic % of carbon decreases. This is in agreement with previous results [44], [45]. Suboch and co-workers reported that a pronounced broadening of the C1s occurs as nitrogen is incorporated [46]. The deconvolution of the N1s XPS spectra showed five components for N-doped N-A-CNT_x corresponding to pyridinic-N (398.5 – 397.6 eV), pyrrolic-N (399.9 – 400.5 eV), graphitic-N (401.4 – 401.5 eV), oxidized pyridinic-N (403.2 – 403.3) and chemisorbed N₂ (405.6 – 405.8 eV), respectively. Since the pyridine-like nitrogen atoms are an essential component in generating bamboo-like structures [47], [48], then the observed results corroborate the TEM images which showed an increased bamboo-like structure with increasing nitrogen content. Moreover, Ayala et al., [49] reported that pyridinic configuration can be responsible for the metallic behaviour in nitrogen doped MWCNTs. This metallic behaviour arises from the delocalized electrons contributed by the formation of the pyridinic configuration.

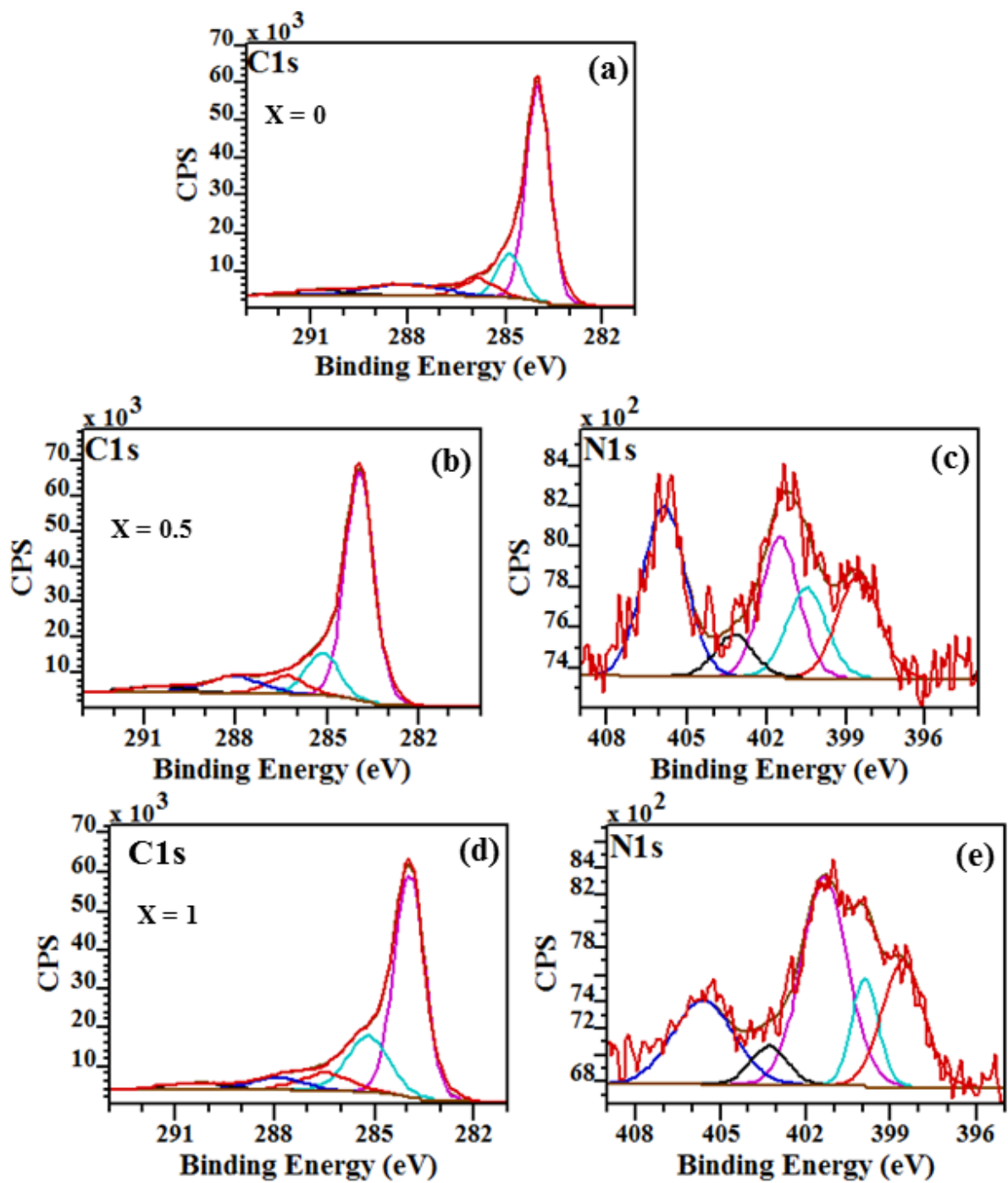


Figure 5-3: The XPS spectra of deconvoluted C1s and N1s peaks of N-A-CNT_x $x = 0$ (a), $x = 0.5$ (b and c) and $x = 1$ (d and e).

5.2.6 Identification of Fe impurities by Mössbauer spectroscopy

The room temperature Mössbauer spectra for the three samples are shown in Figure 5.4. The spectra of all the samples showed the presence of purified iron in both magnetic and non-magnetic phases. The values of the hyperfine interaction parameters for the different spectral components, namely, the magnetic hyperfine field at the iron nuclei B_{hf} , the isomer shift (IS), the quadrupole splitting/shift (QS) and the relative area A(%) of the components, are listed in Table 5.4.

The spectrum for the sample with $x = 0$ shows the presence of two magnetic sextets (SX1 and SX2), a quadrupole doublet (D) and a single line component (S). For SX1, the following parameters were extracted from the fits to the data, IS = -0.21 mm/s, QS = -0.06 mm/s and $B_{\text{hf}} = 20.6$ T and is assigned to cementite (Fe_3C). The spectral component, SX2 with IS, QS and B_{hf} values of -0.07 mm/s, QS = -0.04 mm/s and $B_{\text{hf}} = 33.6$ T, respectively is attributed to the α -Fe phase with a body centred cubic (bcc) structure. The S component with IS = 0.10 mm/s corresponds to the γ -Fe (austenite) phase of metallic iron with a face-centred cubic (fcc) structure and the doublet (D) with hyperfine parameters of IS = -0.12 mm/s and QS = 0.61 mm/s is ascribed to a paramagnetic Fe^{3+} phase. This is consistent with literature where it has been reported that Fe nanoparticles (Fe-NPs) inside MWCNTs produced by pyrolysis are essentially composed of cementite and metallic iron (Fe^0) with a gamma and alpha iron structure [50–52]. The spectra for the two samples containing nitrogen ($x = 0.5$ and 1) were fitted with only one magnetic sextet (SX1) and a quadrupole-split doublet (D) with hyperfine parameters similar to the spectrum for $x = 0$ (see Table 5.4).

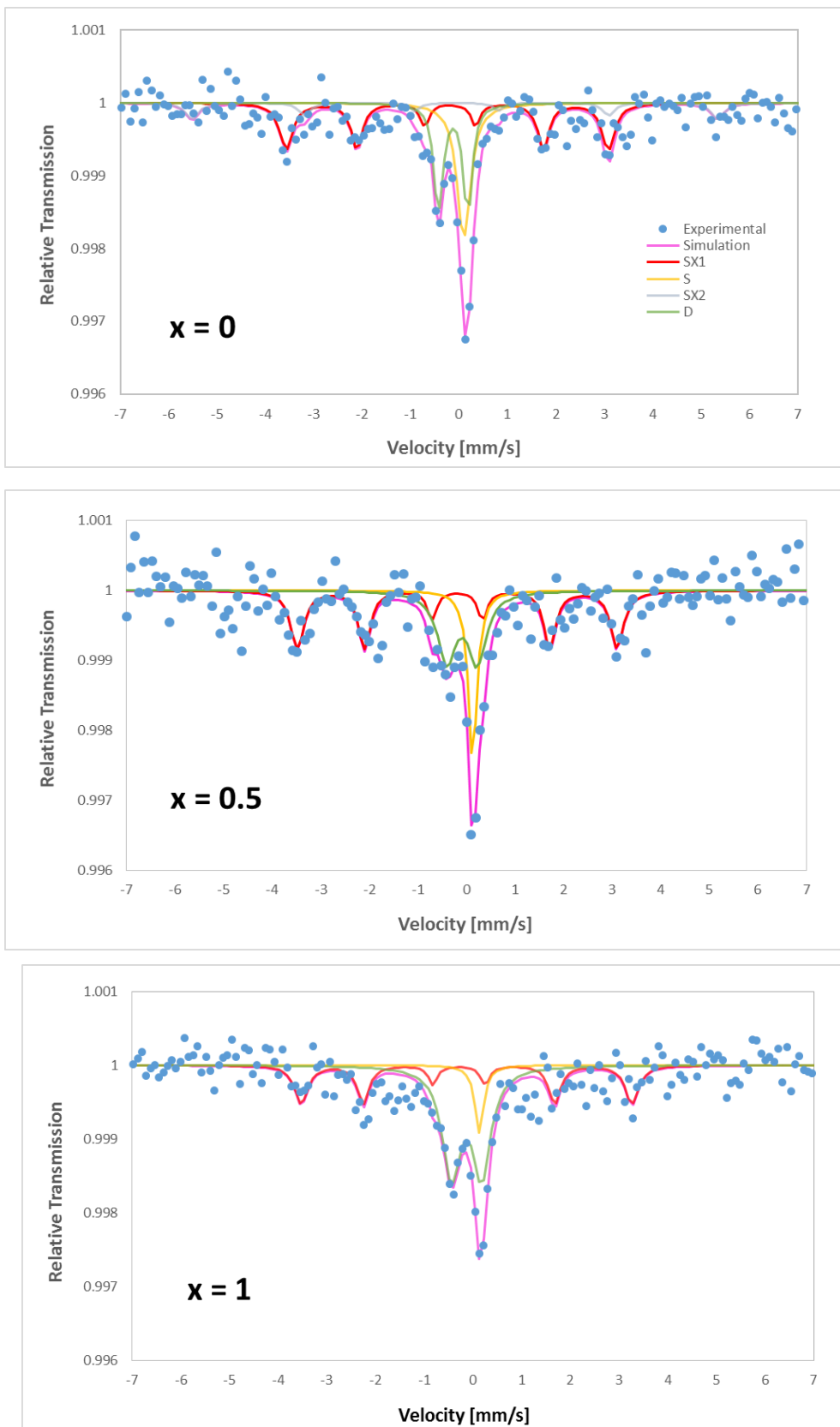


Figure 5-4: Mössbauer spectra of N-A-CNT x ($x = 0, 0.5$ and 1).

Table 5-4: Hyperfine parameters extracted from the Mössbauer for N-A-CNT_x (x = 0, 0.5 and 1).

Comp.	N-A-CNT _x (x = 0)				N-A-CNT _x (x = 0.5)				N-A-CNT _x (x = 1)			
	IS	QS	B _{hf}	A(%)	IS	QS	B _{hf}	A(%)	IS	QS	B _{hf}	A(%)
SX1	-0.21	-0.06	20.6	36.9	-0.19	0.00	20.4	45.6	-0.21	0.16	21.0	33.6
SX2	-0.07	-0.04	33.6	11.7	-	-	-	-	-	-	-	-
D	-0.12	0.61	-	26.4	-0.09	0.63	-	33.9	-0.13	0.62	-	57.6
SL	0.10	-	-	25.0	0.13	-	-	20.5	0.13	-	-	8.8

The predominant spectral components detected in all the samples are Fe₂O₃ (Fe³⁺) and cementite (Fe₃C) and the less prominent components are due to the α -Fe and γ -Fe phases. The α -Fe phase only existed in the pristine N-A-CNT_x (x = 0) with an abundance of ~12%. The Fe₃C content in the three samples was 39 ± 6%. As the nitrogen content increased for x = 0 to x = 1, the proportion of the Fe₂O₃ increased from ~26% to ~58%, while that of γ -Fe fraction decreased from 25% to ~9%. Lyubutin and co-workers [53] reported that the absence of α -Fe in the nitrogen containing carbon nanotubes was related to the effect of nitrogen adsorbed onto the Fe-nanoparticles. The dissociation of acetonitrile over the Fe-nanoparticles produced carbon and nitrogen atoms which can adsorbed onto the iron. The ternary C-Fe-N diagram showed coexistence of γ -Fe, Fe₃C and iron nitride (FeN₃) at 700 °C [54]. The Mössbauer spectra of the nitrogen doped samples (x = 0.5 and x = 1) detected no FeN₃ phase which could be explained in terms of the removal of nitrogen from nanosized metallic particles on cooling of the product. Lyubutin and co-workers reported that nitrogen which dissolved in the iron nanoparticles stabilized Fe₃C and this inhibited the formation of α -Fe [55].

5.2.7 Magnetic properties of N-A-CNT_x

Transmission electron microscope images of Figure 5.1 (b, d and f) on all the aligned carbon nanotubes have confirmed the presence of Fe-based NPs embedded within their cavity after purification. The exact nature of the Fe based NPs have been identified using hyperfine interaction measurements. Thus to determine the magnetic properties of the aligned carbon nanotubes, bulk and surface magnetization of 10mg N-A-CNT_x were measured by direct current (dc) magnetic susceptibility measurement with a SQUID magnetometer. The isothermal magnetization curves for the various nitrogen concentrations are presented as hysteresis loops in Figure 5.5. From this figure, the magnetostatic parameters comprising of the saturation magnetization, M_{sat} , the

coercivity, H_c and the remanence magnetization, M_{rem} have been determined as shown in Table 5.5. The ferromagnetic behaviours shown by the hysteresis for all the aligned nanotubes are predominantly attributed to γ - Fe_2O_3 and cementite Fe_3C NPs identified previously from Mössbauer measurements. The shape of the hysteresis loops further indicate that the magnetization measurements have been carried out below the Curie temperatures of the major constituents; cementite, Fe_3C (483 K) and Fe_2O_3 (900 K).

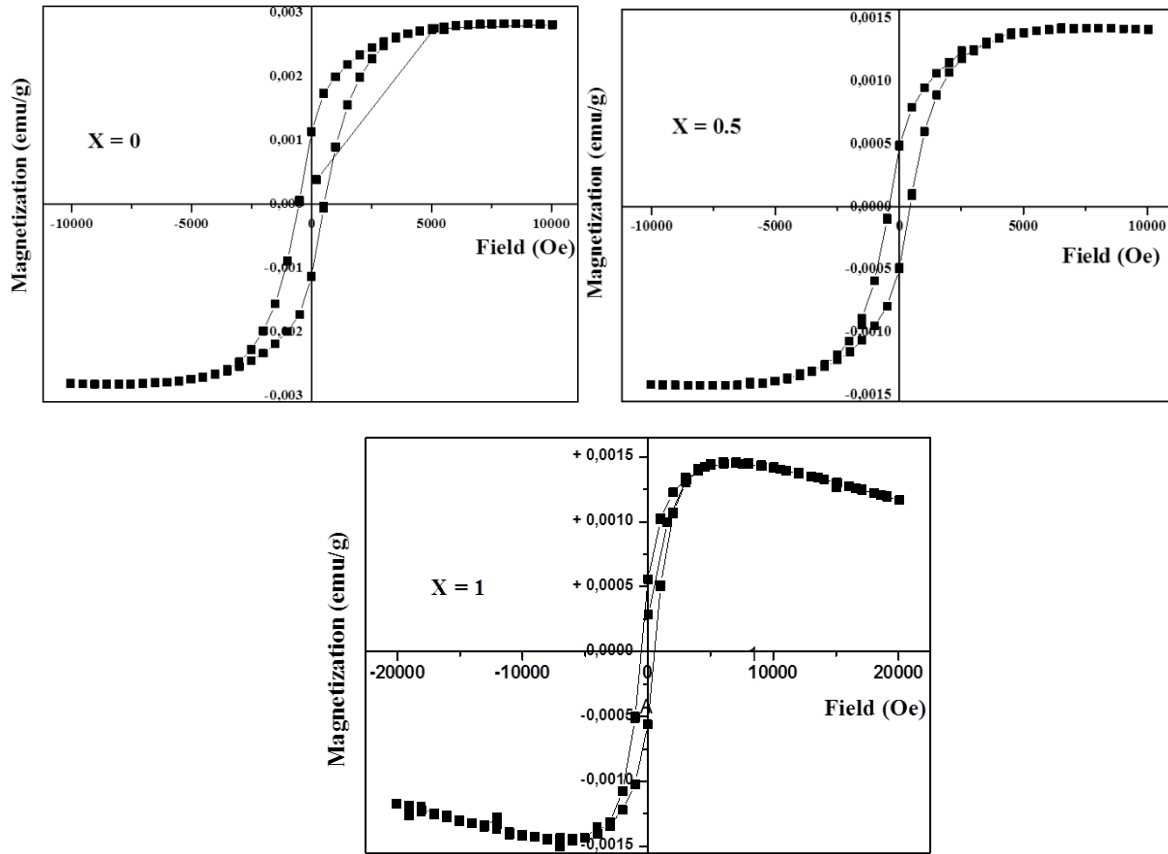


Figure 5-5: Magnetization hysteresis loops of then N-A-CNT $_x$ ($x = 0, 0.5$ and 1) samples.

It is seen in Table 5.5 that the increase in the concentration of N in aligned carbon nanotube increases the coercive field and decreases remanence magnetization. The increase in coercivity is attributed to the changes in the concentration and the average size of Fe NPs present within the MWCNTs. It is evident that higher N concentration introduces bamboo like cavities which restrict the size of Fe-NPs encapsulated in the aligned CNTs. This is further supported by the TGA data of N-A-CNT $_1$ which has the least residue mass and the lowest concentration of small size Fe NPs as collaborated by TEM. The coercivity values measured for all the samples are two orders of magnitude larger than the room temperature values of bulk Fe_3C ($H_c < 100$ Oe), Fe_2O_3 (39 Oe)

and bulk Fe (10e) [58]. This observation underpins the contributions of size effects or single domain particles to the H_c values. However the role of magnetic anisotropy can also not be neglected. The value of H_c for small Fe NPs is determined by the product of its volume and energy [57] and they can be tuned for magnetic storage applications [59].

In terms of magnetization, the values given in table 4 are normalized using the mass of the sample used for SQUID measurements (10mg). Since magnetization is attributed to Fe based compounds it is essential that these values are determined from the proportion (mass) of ferromagnetic NPs present in each sample after purification. Thus the M_s values have been re-calculated to 5.5, 2.2 and 3.3 emu/g for the $x=0, 0.5$ and 1.0 . The values are unusually lower than those observed for bulk iron (222 emu/g). The difference in these saturation magnetization values could be attributed to the uncertainties in the actual determination of the proportions of Fe in the NPs. In addition the small concentration and distribution of Fe NPs in the N-A-CNTs could preclude exchange interaction effects in Fe NPs distributed at distances $R > 100$ nm, which is corroborated from the TEM data.

Table 5-5: Coercivities, remanence magnetization, saturation and squareness values for the hysteresis loops of N-A-CNT $_x$ ($x = 0, 0.5$ and 1).

N-A-CNT $_x$	Length of NPs (R_{NP}) nm	H_c (Oe)	M_{rem} (emu/g)	M_s (emu/g)	M_{rem}/M_s
$X = 0$	200	497	0.0011	0.00282	0.39
$X = 0.5$	50	444	0.0005	0.00141	0.36
$X = 1$	10	522	0.0005	0.00117	0.43

Further it is observed that the remanence values decrease with nitrogen in the embedded ferromagnetic NPs. This observation has been attributed in literature to several competing mechanisms namely; reduced indirect exchange coupling between magnetic NP in CNT ambient, diamagnetic screening in defect free CNT [56] and magnetic anisotropy. In our case the diamagnetic driven mechanism is ruled out for nitrogen doped aligned carbon nanotubes are paramagnetic in nature. Thus the nature of magnetic coupling could be established from the squareness curve which plots the dependence of M_{rem}/M_{sat} with the Fe concentration.

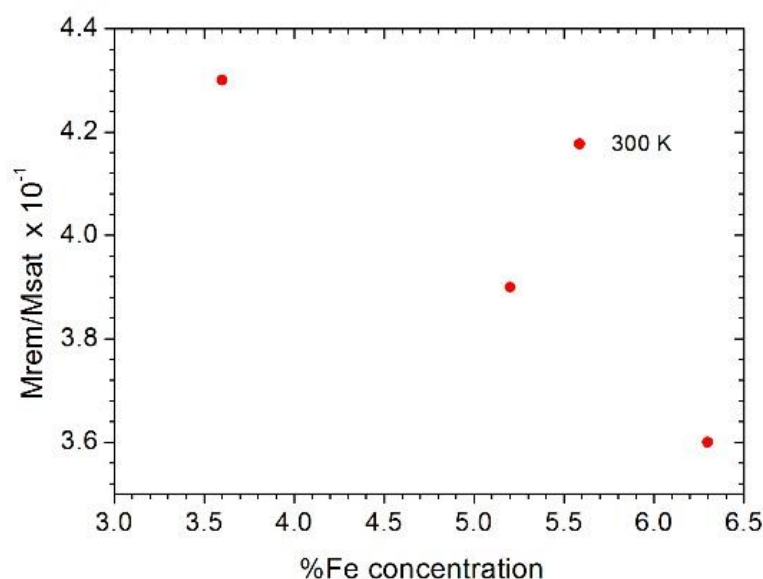


Figure 5-6: Squareness versus the concentration of Fe at room temperature.

It is seen in Figure 5.6 that the squareness (M_{rem}/M_{sat}) at room temperature decreases from 0.43 to 0.36 corresponding to increase in Fe concentrations from 3.6 to 6.3 %, respectively. The drop in the squareness could be due to combined effects of thermal fluctuations and reduced interaction and scatter amongst the NPs. It is seen that the low Fe concentrations correspond to the highest nitrogen concentration and smallest NP sizes.

The temperature dependence of the magnetization for the N-A-CNTx samples is shown in Figure 5.7. The induced moment decreased with increasing temperature. Although Curie temperature cannot be determined from the figures it is clear that it is > 300 K. Since T_c for bulk Fe is 1048 K, the range of the Curie temperature is could be well below the bulk value. This points to either a size dependence [60–62] of the nanoparticles or that the ferromagnetic behaviour is not attributed to pure Fe. However the ferromagnetic - paramagnetic boundary is evident. Its temperature dependence is rather complex and cannot be described by a simple Curie law behaviour of the localized non-interacting spins. Purifying the samples with 55% nitric acid caused a decrease in the magnetic moment as a result of the removal of the magnetic impurities during the purification process [63], [64].

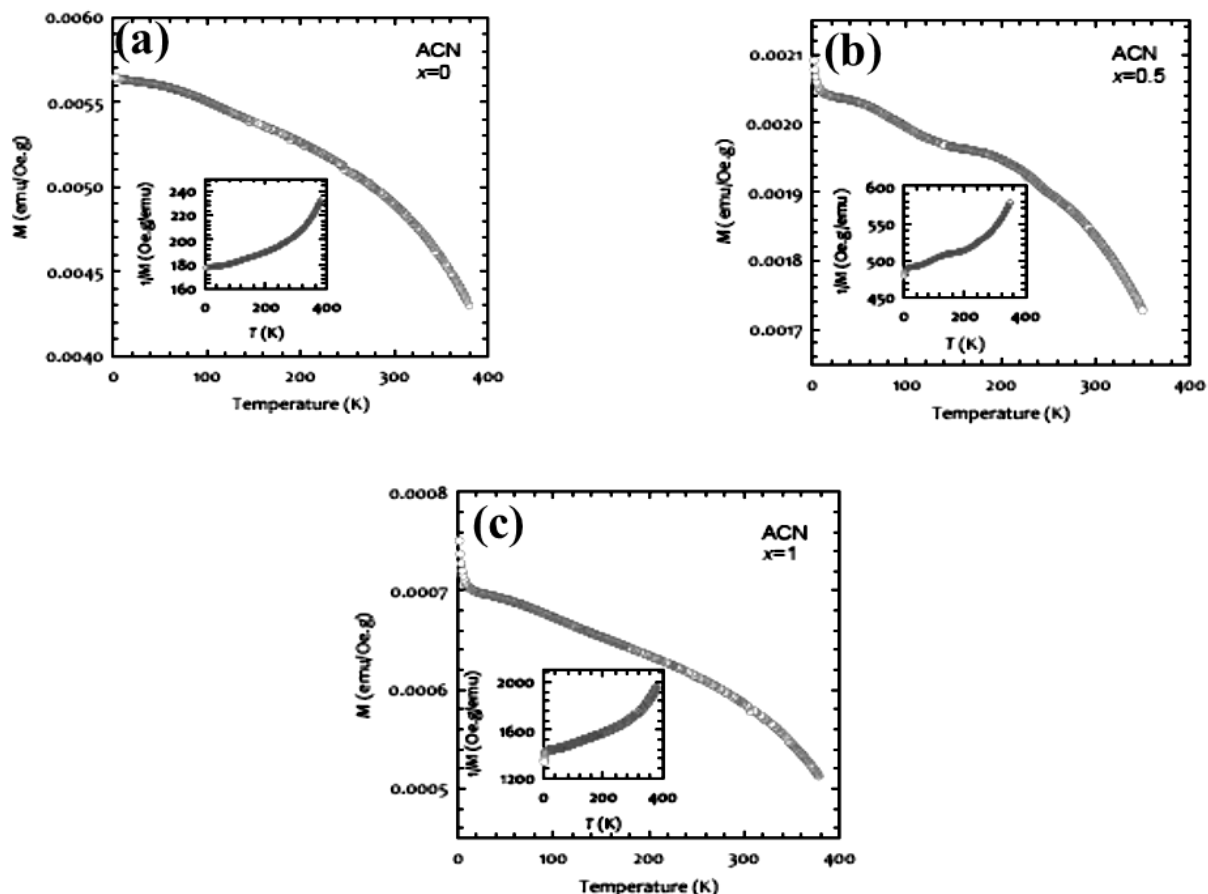


Figure 5-7: Temperature dependence of magnetization for N-A-CNT_x ($x = 0, 0.5$ and 1) measured at $H = 500$ Oe.

5.2.8 Electron paramagnetic resonance (EPR) spectroscopy

Shen and co-workers [66] described three general types of EPR signals that can be observed in CNTs. These signals originate from: 1) isolated unpaired spins owing to impurities or intrinsic CNT defects, 2) conduction electron spin resonance (CESR) from CNTs and/or metallic impurity particles, and 3) a broad electron ferromagnetic resonance (FMR) as a result of residual magnetic catalyst nanoparticles. EPR measurements are known to be sensitive to metal impurities and dangling bond defects [67]. The EPR spectra of N-A-CNT_x ($x = 0, 0.5$ and 1) and their absorption spectra at room temperature are shown in Figure 5.8 and depict a paramagnetic type behaviour. EPR spectra generally show single and broad signals without hyperfine splitting for CNTs [68–70].

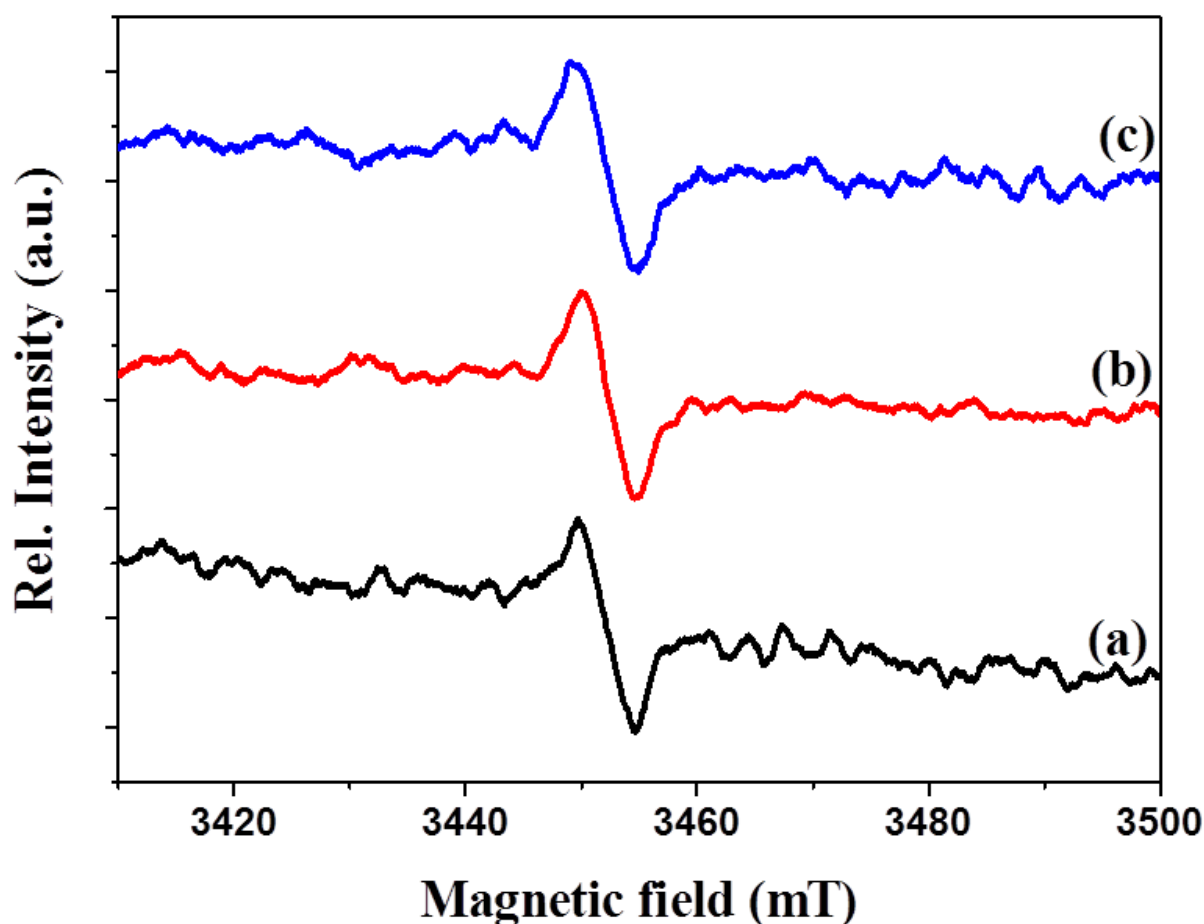


Figure 5-8: EPR spectra of N-A-CNTx; (a) $x = 0$, (b) $x = 0.5$ and (c) $x = 1$.

Kolodiazhnyi and co-workers [71] reported that when a very broad asymmetric EPR feature is observed it can be attributed to a ferromagnetic resonance (FMR) caused by the remaining catalyst nanoparticles after purification, which in our case is consistent with the TGA, TEM and dc susceptibility results. The dipolar broadening arises from the magnetic interactions between the unpaired electrons present in the multiwall CNTs [72]. The defects in the nanotubes contribute significantly to the broad line shape of the EPR spectra and modify the g -values depending on the type of defects present [68], [69]. This is seen in this case for the remaining nanoparticles present after the purification process. The g -value is ca. 2.0021 for all the samples and it is significantly similar to the value of free electron [67]. Many unpaired electrons were generated on the CNTs as is evident from the strong EPR signals [73], [74]. Clewett and co-workers reported that these signals are associated with localized spins caused by the acid treatment during the purification [75], implying that many unpaired electrons were generated on the CNT surface [72]. The increase in these signals is attributed to extrinsic and/or intrinsic point defects in the CNTs after purification, as has been reported by other authors [76]. Scanning the entire range of magnetic

fields shows that the EPR signals are due to the presence of Fe-nanoparticles in all the samples. The nitrogen concentration could not be determined from the ESR data as a result of the weak signals.

5.3 Conclusions

Aligned MWCNTs produced from ferrocene and toluene/acetonitrile mixtures were synthesized and purified by 55% nitric acid. TGA analysis indicated the presence of Fe-impurities of between 3 and 6% remaining in the purified sample. SEM and TEM analysis indicated that bundle thickness, outer diameter and wall thickness decreased with nitrogen concentration, while the inner diameter increased. TEM images also indicated an improved bamboo structure with increasing N-content. The I_D/I_G ratio and FWHM values increased with increased nitrogen content. This indicates that more disorder and defects are introduced into the CNT lattice on N doping. We were able to show that the Fe-impurities are made up mostly of Fe_2O_3 , Fe_3C , α -Fe and γ -Fe from the residues embedded within the N-A-CNTx tubes. Magnetic properties of N-A-CNTx were shown to depend on the Fe-residue embedded within the tubes and this was confirmed by SQUID analysis. The Fe-residue was predominantly made up of Fe_3C and Fe_2O_3 for the nitrogen doped containing samples ($x = 0.5$ and 1) as determined from Mössbauer spectra. The ferromagnetic content of the Fe nanoparticle residue decreased with increased nitrogen content while the paramagnetic doublet (Fe^{3+}) component increased with increased nitrogen content. All the samples exhibited magnetic properties (ferromagnetic behaviour). As the nitrogen content increased the M_s values decreased. The magnetization M decreased with increasing nitrogen content. The levels of purification of the samples determined by both EPR and dc susceptibility measurements are in reasonably good agreement, as both methods are very sensitive to magnetic impurities.

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Chapter 6: Properties of C-GaN nanostructures for sensor applications

6.1 Introduction

GaN is a wide-band gap (3.39 eV at 300 K) semiconductor with excellent thermal stability and optoelectronic property [1]. These unique combination of properties have seen it been considered as a promising candidate to revolutionize applications in optoelectronic devices. Indeed it was the prominent material that was used in the fabrication of blue light emitting diodes (LEDs) with high quantum efficiency [2], laser diodes [3]. Besides it has exhibited quantum confinement effects enabling it to be fabricated as zero-dimension quantum dots [4], two-dimension quantum wells [5]. Despite the numerous applications as electronic devices, there is limited literature of the application of GaN as a sensor device which operates in dynamic temperature ranges. Therefore a renewed emphasis has emerged on the fabrication of robust solid-state sensors capable of detecting chemical, gas, biological or radiation. GaN-based solid-state sensors have been used for these applications. The nature of the sensor response has varied considerably depending on the material properties. As such it spans from changes in the drain-source current due to piezoelectric polarization of the induced 2D electron gas in AlGaIn/GaN based high mobility sensors. Doping also provides a pathway towards the application of III-V semiconductors for gas sensing. Among these include Si-doped GaN epilayer which have been used for H₂ sensing at 50 °C [6]. Additionally, GaN nanostructures were applied as H₂ gas sensors at elevated temperatures (300 °C) [7]. The GaN-based devices thus appear promising for a wide range of chemical, biological, combustion gas, polar liquid, strain and high temperature pressure-sensing applications. Furthermore these sensors are compatible with high bit-rate wireless communication systems that facilitate their use in remote arrays.

The doping of GaN with carbon and subsequent effects on the electronic and thermal properties are reported in the literature. These limited and unsuccessful attempts have encompassed the intentional incorporation of carbon into GaN lattice to form p-type GaN. Additionally C doping to produce semi-insulating GaN for applications in high electron mobility transistors (HEMTs) have also been reported [8]. The C sites in GaN lattice have been identified with substitution of Ga or N sites in GaN, however the stability of these defects in these sites is predominantly

determined by their formation energies. Lyons *et al* have adduced that carbon is most stable on the N site (C_N) based on similar atomic size considerations. Nevertheless, this requirement is not necessary and sufficient since the site preference of carbon is determined by the following;

- relative abundance of Ga and N, i.e.,
- on the Ga and N chemical potentials and lastly
- on the Fermi level and defect formation energies [9].

A number of theoretical and experimental studies have reported the substitution of carbon into the N site have resulted in the formation of passivated shallow acceptors, C_N [8 – 16]. Wright reported that carbon substituted on the Ga (C_{Ga}) site acts as a shallow donor and C_N to be a shallow acceptor [10]. Wright predicted that C_N should readily form in n-type and C_{Ga} in p-type GaN as a compensating species. Compensation of C_N acceptors by C_{Ga} is predicted to occur in C doped GaN grown under N-rich conditions. Thus material modification provides an accessible route to tailor the surface electronic properties for a diversity of versatile applications. Among these applications include robust sensing of chemicals, gases and radiation in high temperature and extreme ambient. This is evident by the spontaneous and piezoelectric polarization-induced surface and interface charges which are currently used in the development of highly sensitive and robust sensors for gas, polar liquids and mechanical pressure detections. Surface symmetries influence the adsorption sites and orientation of organic molecules in the first monolayer [11], [12]. The surface symmetry is a vital property for controlling the properties of materials as well as their surface reconstructions [13], [14]. Yang and co-workers have carried out experimental work on carbon-coating of GaN using amorphous carbon [15] by using carbon coated GaOOH nanospindles as precursors. This chapter presents attempts at C-doping- and coating of - GaN and explores the resulting properties with a view for application of these materials as active layers in gas sensors.

6.2 Results and Discussion

The four samples were named according to the carbon source gas and inert gas that were used. They were called C-GaN CN (acetylene as carbon source and nitrogen as a carrier gas), C-GaN CA (acetylene as carbon source with argon as a carrier gas), C-GaN TA (toluene as carbon source and argon as a carrier gas) and C-GaN TN (toluene as carbon source and nitrogen as a carrier gas). These acronyms will be subsequently used in this chapter.

6.2.1 Powder X-ray diffraction (PXRD) analysis

The phase and structure of the GaN grown at 1100° C and C-GaN nanostructures grown at 600 °C respectively were examined by X-ray powder diffractions (XRD) using the Bragg Brentano geometry as shown in Figure 6.1. The XRD pattern were recorded using Cu K α radiation. All the diffraction peaks were indexed to the wurtzite structure. The absence of a Bragg reflection associated with the presence of free standing C at $2\theta = 25^\circ$ in GaN implies the possible substitution of N with C in the GaN lattice. The substitution process could lead to strain and charge defects. However the presence of carbon in the amorphous phase cannot be ruled out from the XRD patterns, therefore this argument was further evaluated using Raman spectroscopy.

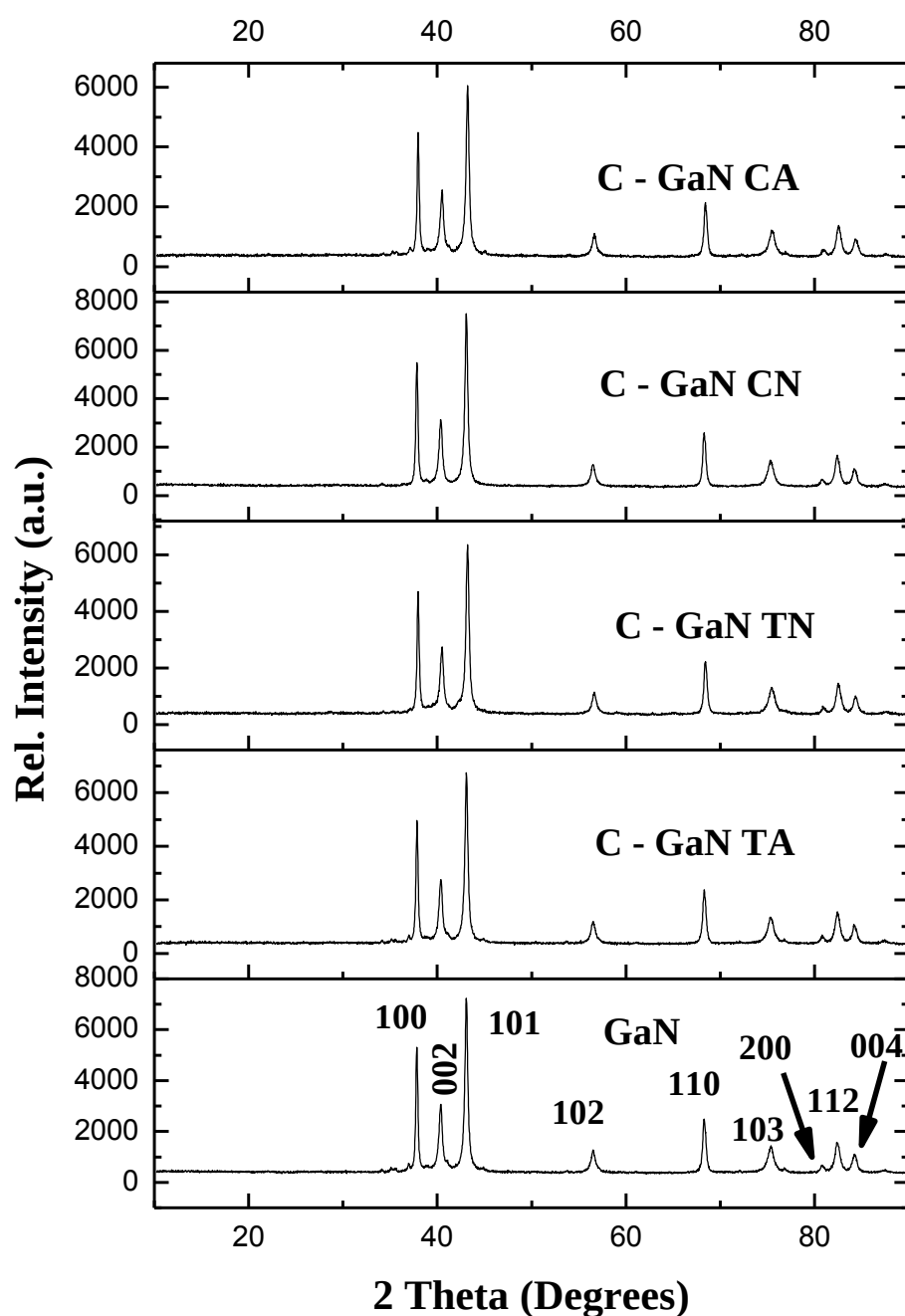


Figure 6-1: XRD patterns of GaN and C-GaN. The crystallite sizes of the GaN and carbon doped nanostructured materials were analysed using the Debye-Scherrer equation to 19 nm.

6.2.2 Morphology of GaN and carbon coated GaN (C-GaN)

6.2.2.1 Morphological studies using SEM and TEM analysis

The morphology and structure of the GaN and C-GaN nanostructures were studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 6.2(a) displays

the low magnification SEM images of GaN nanoparticles, whereas figure 6.2(b) depicts the high magnification SEM images of GaN nanostructures synthesised at 1100 °C. The low magnification SEM image shows that the nanoparticles are agglomerated. The high magnification SEM image shows randomly oriented rod and sheet-like structures. The agglomeration of the nanoclusters is due to van der Waal interactions between the particles [16]. Increasing the magnification reveals the structures to be rod and sheet-like. Figures 6.2c to 6.2f depict the SEM images of the carbon coated samples C – GaN TA, C – GaN TN, C – GaN CA and C – GaN CN respectively synthesised at 600 °C. The images show a mixture of rods, sheet-like and nanoparticle clusters at high magnification.

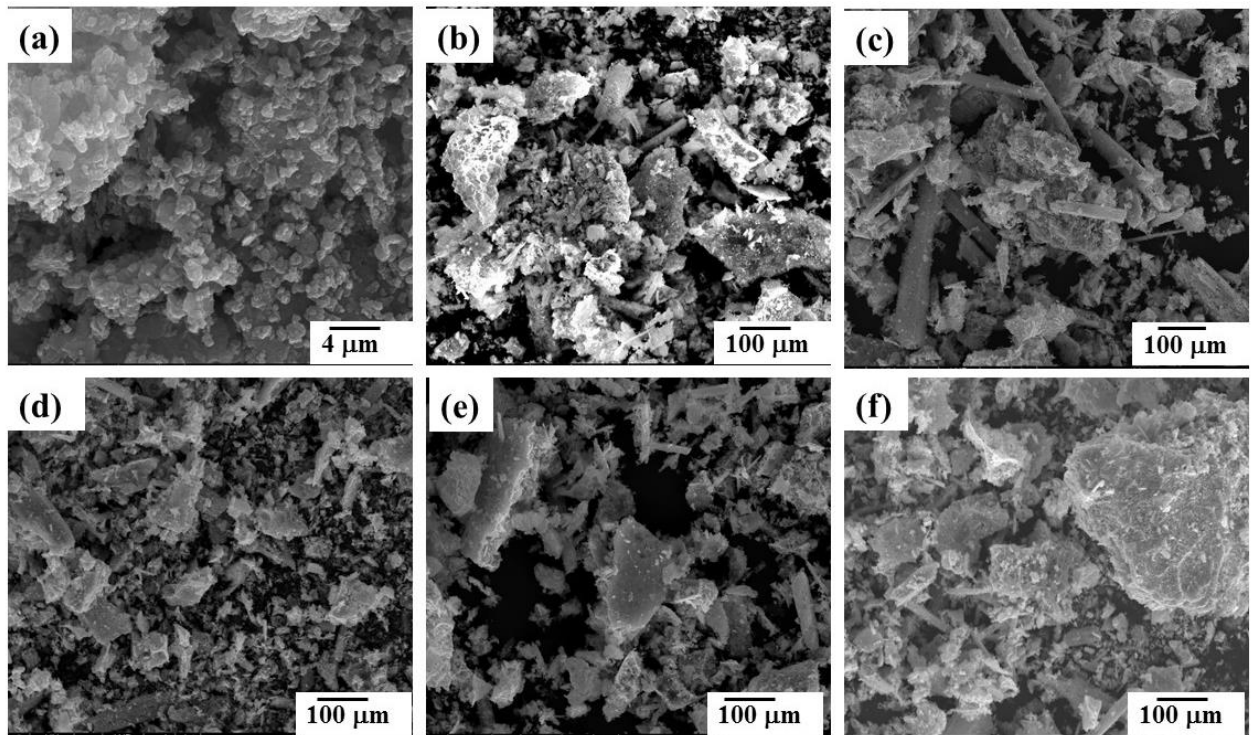


Figure 6-2: SEM images of (a) low mag. GaN, (b) high mag. GaN, (c) C-GaN TA, (d) C-GaN TN, (e) C-GaN CA, and (f) C-GaN CN

TEM analysis

The TEM images of GaN decorated nanostructures are presented in Figure 6.3 with different magnifications. Figure 6.3(a) shows rod – like particles with an irregular morphology which on increased magnification confirms the formation of GaN sheet like surfaces as shown in figure 6.3(b).

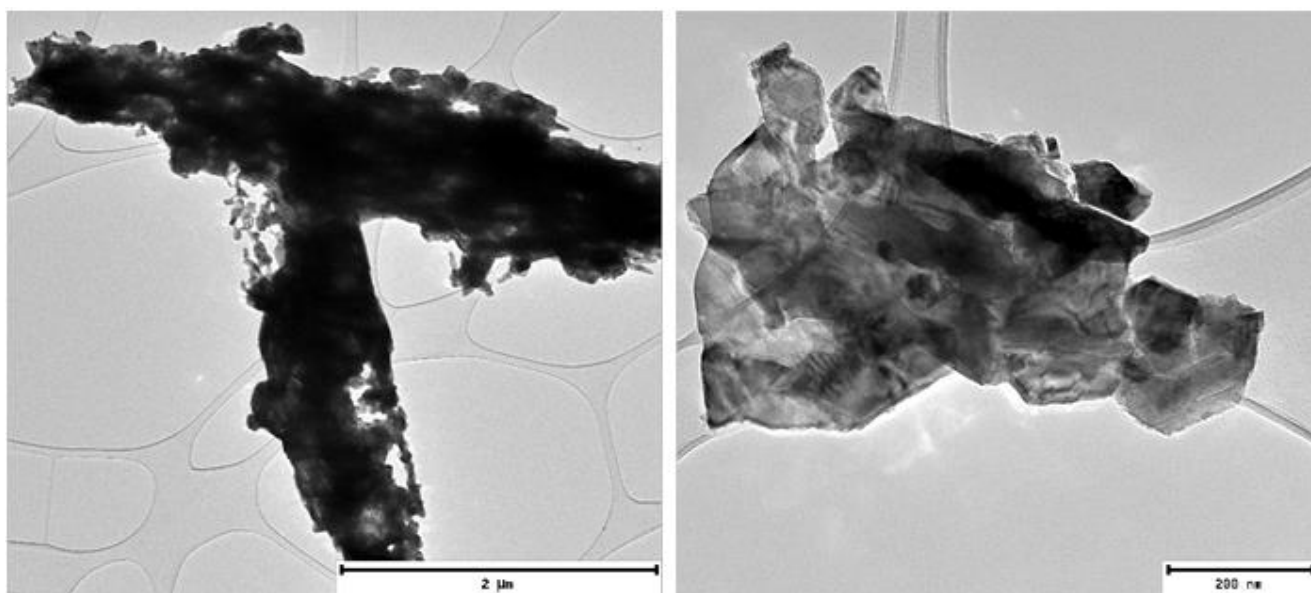


Figure 6-3: (a and b) TEM images of GaN synthesised at 1100 °C.

6.2.3 Thermal gravimetric analysis (TGA)

The operation of a sensor at elevated temperatures and under extreme environments requires that the active layer be thermally stable and chemically inert. In this respect, TGA has been used to determine the thermal stability and composition of carbon in C – GaN. Nanostructure GaN material was first synthesised at 1100 °C for *exsitu* doping with C. Figure 6.4 shows the TGA profiles run in air of C – GaN samples prepared at 600 °C. It was observed that there is about 3.9, 9.7, 9.9 and 4.1 % weight of carbon in C – GaN CN, C – GaN CA, C – GaN TA and C – GaN TN respectively (see Table 6.1). These profiles further show that the samples synthesized with argon as a carrier gas have higher carbon content on the GaN lattice and this confirmed by the high decomposition temperature which scales with the bond enthalpy of Ga-C/N. Figure 6.4 (a and b) also presents distinct TGA profiles for C-GaN synthesized with argon (C-GaN TA and C-GaN CA) and with nitrogen gas (C-GaN TN and C-GaN CN) as carrier gases, respectively. The samples C-GaN TA and C-GaN CA show an initial weight loss starting at about 500 °C. The two other samples TN and CN show a steady decrease up to 754 and 737 °C, respectively. There are three thermal decomposition temperatures in C-GaN CN namely 331, 466 and 489 °C. The samples C-GaN TN and C-GaN CN have lower decomposition temperatures, indicating that there is more defects and structural disorder; however a precise qualitative confirmation is obtained from Raman Spectroscopy measurements which appear in subsequent sections. Since the time of reaction is the same for all the samples this could be attributed to the type of carrier gases and the flow rate used

during the doping of the carbon. The role of the carbon source remains insignificant. For example, the samples that used nitrogen as carrier gas (C-GaN CN and C-GaN TN), one of the sample that used toluene as carbon source (C-GaN TA) has slightly more carbon deposited on it compared to the other one that used C_2H_2 as carbon source. The same scenario applies for the samples that used argon as a carrier gas (C-GaN CA and C-GaN TA). This could be because toluene has more carbon in its structure compared to C_2H_2 . The type of carrier gas plays a significant role in the coverage of carbon on GaN. From table 6.1 it can be seen that the use of Ar as a carrier gas leads to the deposition of more carbon on the GaN irrespective of the carbon source due to their high decomposition temperatures. This is indeed puzzling as the partial pressure of both carrier gases was constant.

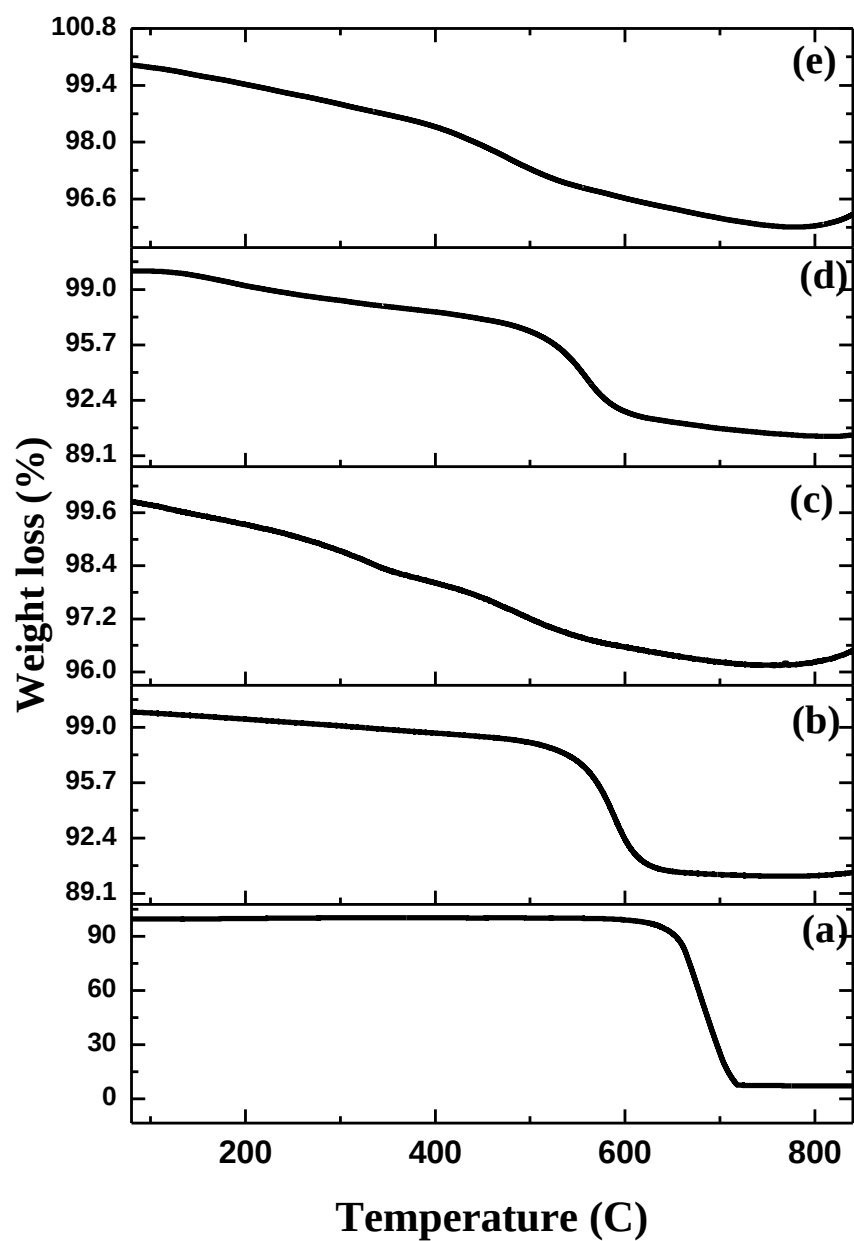


Figure 6-4: TGA decomposition profiles of (a) GaN, (b) C-GaN TA, (c) C-GaN TN, (d) C-GaN CA, and (e) C-GaN CN nanostructures.

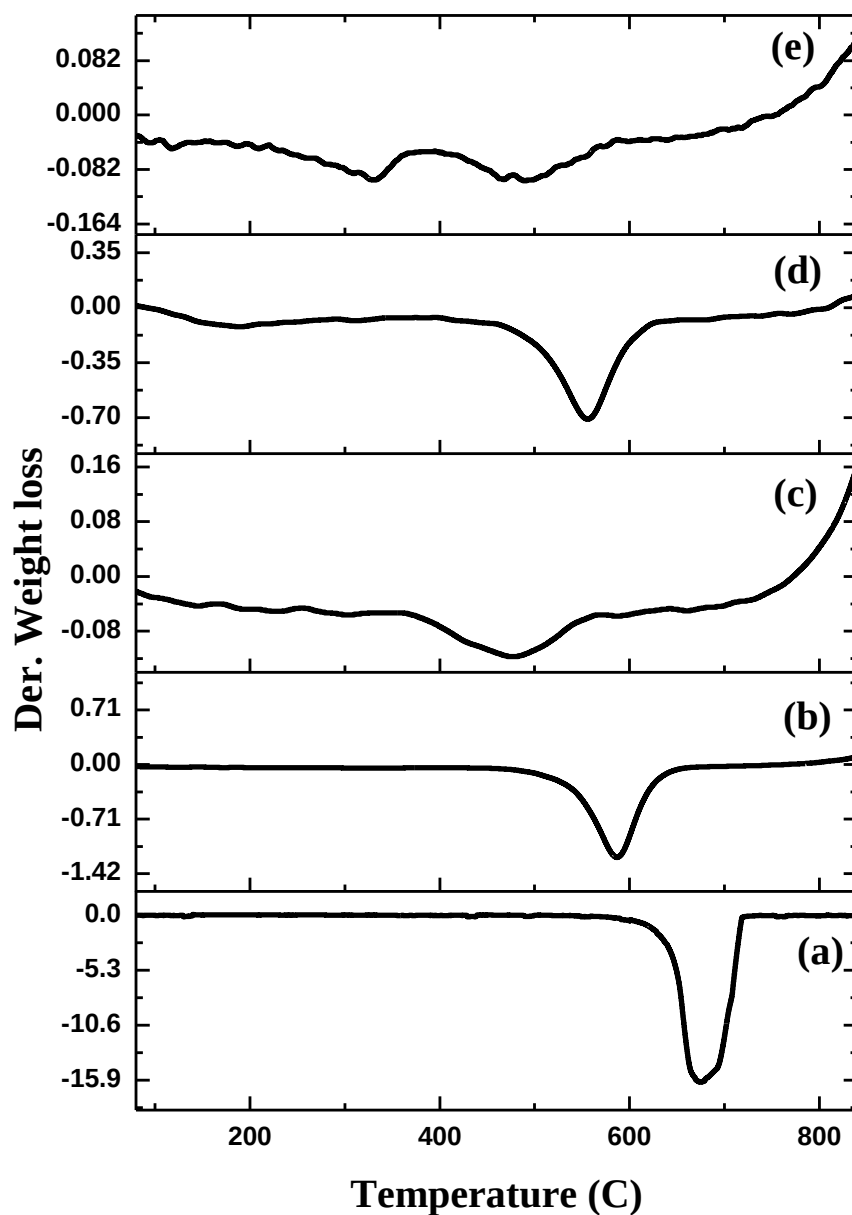


Figure 6-5: TGA derivative profiles of (a) GaN, (b) C-GaN TA, (c) C-GaN TN, (d) C-GaN CA, and (e) C-GaN CN nanostructures.

Figure 6.5 shows that the loss in mass is much higher in samples prepared with Argon as the carrier gas, it is possible that we have defects that are not passivated by Ar thus leading to more material loss than in samples made with N as a carrier gas. In the latter case, N can be used to compensate for the vacancies or defects present. This could be supported partially by the low formation energies of N defects over Ga and C. Similarly the gradual change or loss in mass could be

indicative of oxidation in C-GaN – CN and C-GaN–TN, whereby a higher reactivity of the oxygen species on the surface is expected compared to that of N and C. This is further supported by the high enthalpy of the Ga-O (353.5 kJ/mol) compared to Ga-Ga (112 kJ/mol) and Ga-N as well.

Table 6-1: Residual mass and thermal stability temperatures of C – GaN samples.

Sample	Residual mass (%)	Decomposition temperature (°C)
C – GaN CN	3.9	331, 466, 489
C – GaN CA	9.7	556
C – GaN TA	9.9	590
C – GaN TN	4.1	475

6.2.4 Raman spectroscopy analysis

GaN in the stable state has a wurtzite structure of space group C_{6v}^4 for which 4 Raman active modes represented by the A_1 , E_1 , and E_2 . The A_1 and E_1 modes split into longitudinal (LO and transverse (TO) components. Figures 6.6 (a) shows the typical room temperature Raman spectra of GaN and C-GaN nanostructures consisting of the phonon modes.

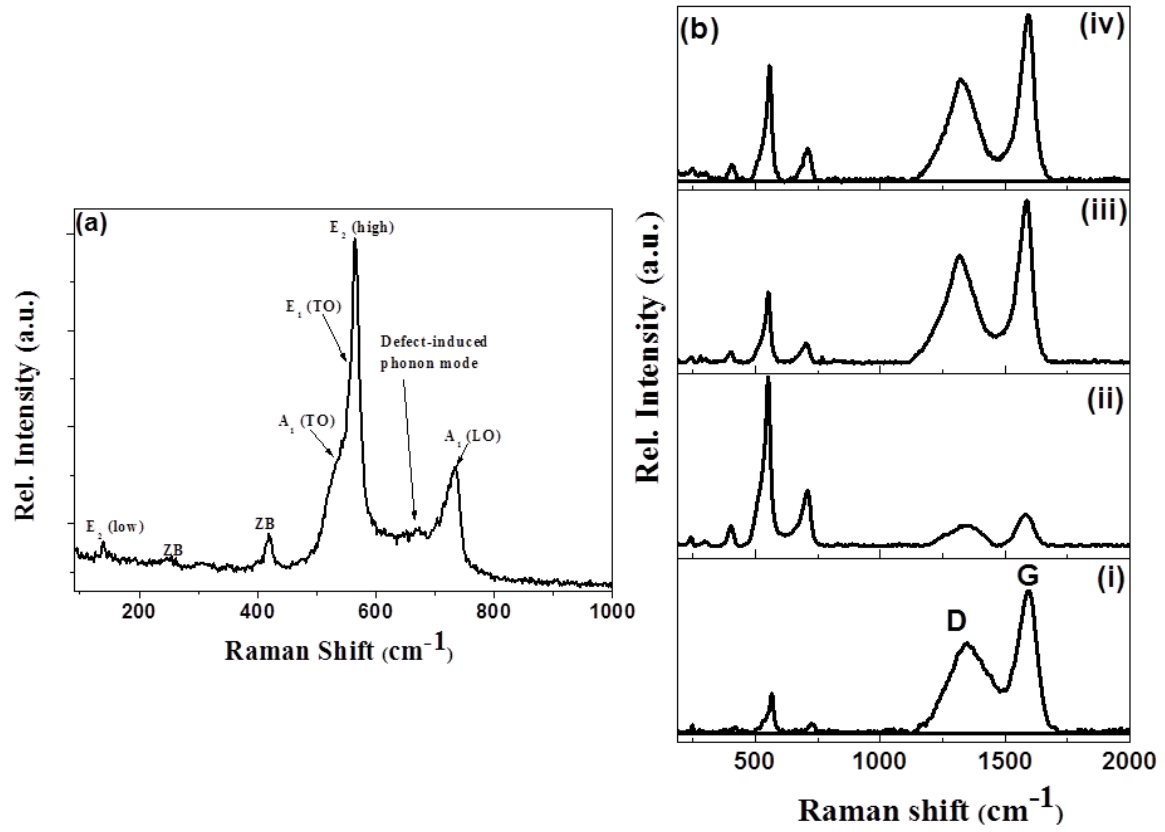


Figure 6-6: Raman spectra of (a) GaN and (b) C-GaN: (i) C-GaN TA, (ii) C-GaN TN, (iii) C-GaN CA, and (iv) C-GaN CN nanostructures.

Table 6-2: Raman modes of bulk and the corresponding experimental samples.

Sample	E ₂ (Low)	ZB	ZB	A ₁ (TO)	E ₁ (TO)	E ₂ (High)	A ₁ (low)
Bulk GaN	144	-	-	533	561	569	735
GaN, this work	143	260	423	530	562	568	738
C – GaN TA	143	248	423	-	556	561	726
C – GaN TN	134	244	404	-	553	558	711
C – GaN CN	140	249	409	-	558	553	712
C – GaN CA	135	247	403	-	552	553	705

Table 6-3: D and G bands of C – GaN as well as their ID/IG ratios.

Sample	Carbon source	Carrier gas	D – band (cm ⁻¹)	G – band (cm ⁻¹)	I _D /I _G
C – GaN CN	C ₂ H ₂	Nitrogen	1330	1587	0.586
C – GaN CA	C ₂ H ₂	Argon	1323	1579	0.620
C – GaN TA	Toluene	Argon	1361	1589	0.622
C – GaN TN	Toluene	Nitrogen	1341	1581	0.580

Figures 6.6 (a) and (b) shows the Raman spectra of GaN and C-GaN respectively. GaN phonon modes are expressed as $A_1(z) + 2B_1 + E_1(x,y) + 2E_2$, where x,y,z refer to the direction of the phonon polarization directions. A_1 , E_1 and E_2 modes are Raman active whereas the two B_1 modes are Raman inactive [17]. The GaN spectrum clearly shows prominent phonon modes at ~ 143 , 260, 423, 562, 568 and 738 cm⁻¹ using Ar⁺ (514.5 nm) excitation. The peaks at 143, 568 and 738 cm⁻¹ are assigned to E_2 (LO), E_2 (High) and A_1 (LO) respectively. The absence of a peak at 150 cm⁻¹ which is associated with defects and their electronic excitations is consistent with their temperature dependence. The observation of this signal is only possible at low temperatures and low activation barriers in the range between 10-60 meV. The symmetry of the most intense peak at 568 cm⁻¹ reflects the hexagonal wurtzite phase of GaN. The peaks 260 and 423 cm⁻¹ were assigned to zone boundary phonons [18]. Sahoo et al., claimed that the two extra peaks observed at ~ 260 cm⁻¹ and 423 cm⁻¹ in the synthesised GaN nanostructures made the possibility of any impurity contaminant effect seems extremely unlikely [19]. There is a shift to the lower side of A_1 (LO) peak compared to the synthesised GaN as indicated in Table 6.2 for almost all the Raman modes. The shift is between 12 and 33 cm⁻¹ compared to GaN. This could be attributed to the incorporation of carbon on the (surface) of the lattice of GaN structure. This also results in the disappearance of Raman mode A_1 (TO). Raman mode A_1 (TO) disappears with carbon doping for all the carbon doped samples. This could be because of the carbon deposited on the surface of the GaN.

The Raman spectra of C-GaN nanostructures shows a further disturbance, indicating the presence of defects within the hexagonal graphitic structure. In addition to the characteristic bands of GaN, the spectrum of C-GaN shows the fundamental D and G bands of carbon. The G band is attributed to the graphitic carbon while the D band indicates the presence of defects within the hexagonal GaN structure. The D and G bands of C-GaN synthesised at 600 °C as well as the I_D/I_G ratios are

shown in Table 6.3. There is an increase in the I_D/I_G ratio with the carbon doping. This indicates that there is more disorder in the carbon present on the surface of the GaN due to the doping. The I_D/I_G ratio of the carbon deposited with argon as a carrier gas is more compared to the one with nitrogen as a carrier gas. This could be because more carbon is deposited with argon as a carrier gas than nitrogen. This correlates with TGA whereby more carbon is deposited with argon as a carrier gas.

6.2.5 Photoluminescence (PL) of GaN and C-GaN nanostructures

The optical properties of GaN are important in optoelectronic applications which can be driven by either electronic or vibration excitations of the defects levels. To determine the nature and the effect of the carbon incorporation in GaN, photoluminescence spectroscopy was carried out and the results are presented in Figure 6.7. Figure 6.7 shows the photoluminescence (PL) spectra of GaN and C-GaN nanostructures recorded at room temperature using a 229 nm excitation from a He – Cd laser. The PL spectra shows two prominent peaks for GaN corresponding to the near band-edge emission (NBE) peak at 3.39 eV and a yellow luminescence (YL) peak at 2.20 eV. The YL emission is sensitive to the quality and purity of the GaN sample. In this respect, several authors have attributed the deep level state associated with the YL emission to Ga vacancy complexes, and it is further supported by their low formation energies (1.1eV) [20], [21], [22]. Reshchikov and co-workers reported that the NBE is attributed to annihilation of free excitons and YL is caused by transitions from the conduction band to a deep acceptor involving a gallium vacancy [23]. However a clear consensus lacks on the origin of the YL emission, as seen by the assertions of Santana-Rodriguez et al., who associate the YL at 2.2 eV with Ga and N vacancies and deep level impurities or structural defects [24]. What is also further clear is that the YL emission does not arise from C doping. The NBE peak is prominent in all the samples. From Figure 6.7 it can be seen that the intensity of the YL peaks for all the samples containing carbon is quenched by carbon addition as compared to emission in pristine GaN. This could be due to carbon incorporation into the GaN lattice. Armitage et al., suggested that carbon related defects caused the YL band in carbon doped GaN, while a gallium vacancy is responsible for the YL band in undoped GaN [25]. Lyons et al attributed the YL to C_N defects [9] whereas Demchenko et al. attributed it to $C_N O_N$ complex [26]. Ogino and Aoki proposed that YL is attributed to a complex consisting of gallium vacancy, V_{Ga} next to C_N [20].

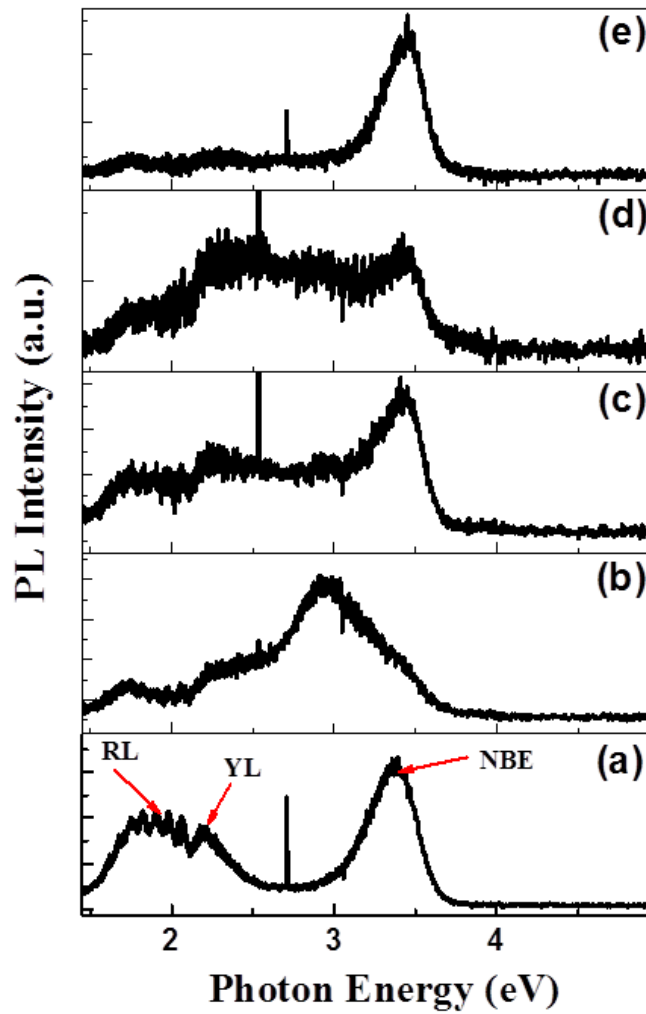


Figure 6-7: Photoluminescence plots of (a) GaN and (b) C-GaN TA, (c) C-GaN TN, (d) C-GaN CA and (e) C-GaN CN nanostructures.

The YL and NBE bands extracted for all the samples are indicated in Table 6.4. From Figure 6.7 it is seen that the NBE peak for C-GaN TA is broad. It's YL and NBE bands have both been red shifted to the lower energy side. The red shift in the YL peak for C-GaN CA is attributed to the presence of shallow defect levels. Both samples used argon as a carrier gas.

We did not observe the presence of blue luminescence (BL) which is at about 2.86 eV in all the samples as reported by other authors [27]. Seager and co-workers observed BL in carbon doped GaN when the doped carbon concentration is high [28]. This could be because the content of the doped carbon in GaN is very small or that the amount of nitrogen related defects is above threshold.

Table 6-4: Respective peaks of YL and NBE of GaN and C – GaN samples

Sample	NBE (eV)	YL (eV)
GaN	3.39	2.20
C – GaN CN	3.45	2.29
C – GaN CA	3.43	2.34
C – GaN TA	3.24	1.75
C – GaN TN	3.43	2.27

From table 6.4 it is observed that there is a slight shift of both YL and NBE peaks when carbon is incorporated into the GaN structure and this is consistent with the XRD data which induced strain through the shift in the Bragg reflexes. The YL bands for C – GaN CA and C – GaN A8 has been observed to have shifted more. The slight shift in the NBE depends on the gas used during the synthesis. Also the intensity of the YL decreases as carbon is incorporated into the structure of the hexagonal GaN. The peak position of the YL of both samples that used argon as a carrier gas have both shifted slightly. The one with C₂H₂ as carbon source has shifted to the upper side while the one with toluene as carbon source has shifted downwards. This could be attributed to the possible electron phonon coupling of the A₁ (LO) and E₁ (LO) modes which could plausibly increase with the substitution of more carbon into GaN lattice.

6.2.6 X-ray photoelectron spectroscopy (XPS) analysis

XPS was used to determine the content and relative ratio of different elemental groups within the C-GaN samples as shown in Figures 6.8 - 6.11. The results of the binding energies and the elemental components are summarised in Tables 6.5 - 6.6. Table 6.5 further shows that the main components are Ga, C, N and O with XPS peaks at the locations of Ga2p_{3/2} (1116.5 – 1116.9 eV), Ga2p_{1/2} (1143.4 – 1143.7 eV), Ga3d (18.6 – 18.8 eV), C 1s (281.6 – 285.7 eV), N 1s (394.6 – 398.7 eV) and O 1s (529.6 – 533.7 eV). The samples were exposed to air hence the detection of impurities like carbon and oxygen. However, the high amount of carbon on the surface does not emerge from air but mostly from the doping, as the XPS spectra of the C 1s core levels indicate. The C1s peak is due to adventitious carbon (taken as 284.6 eV) was used for calibration [29]. Most of the carbon is derived from the C-coating on the GaN surface, however the presence of C in GaN lattice cannot be ruled out. This could solely be the reason for the high carbon concentration (Table 6.6) since the broad I_G and I_D peaks in Raman also indicate the presence of carbon physically

attached to the GaN nanostructure and not chemically bonded to it. More carbon content could imply thicker covering of the GaN surface layer, hence the energy shift is more in the case where the thickness is more with respect to that of pure GaN. From table 6.5, it can be seen that the higher the carbon content the lower the binding energy of Ga2p, N 1s, O 1s and C 1s core levels. This is consistent for all the three samples. There is a significant shift in the BE of sample C2 with the highest carbon content on the surface of GaN with respect to pure GaN compared to the other samples. This is also consistent for all the three samples. These values are towards the lower or higher band of the respective energies compared to pure GaN. The C1s peak has been deconvoluted into five components with the binding energies 283.6 – 283.7 eV (sp^2 carbon), 284.2 – 284.7 eV (sp^3 carbon C-C), 285.1 – 286.0 eV (sp^3 carbon C-N), 285.8 – 286.2 eV (O-C=O) and 287.9 – 288.8 eV (O-C peak) [30], [[31], [32], [33], [34]. The main peak of the C1s at 284.6 eV is due to sp^2 carbon atoms [35]. This is associated with the graphite structure of the carbon [36]. From the deconvoluted spectra the core level spectra of Ga3d appears at about 18.6 – 18.7 eV which corresponds to Ga metal [37]. No peak of Ga 3d appears at 20.8 eV, so there is no Ga–O bonding [23], [24], [25] and the presence of oxygen is in a chemical adsorption state.

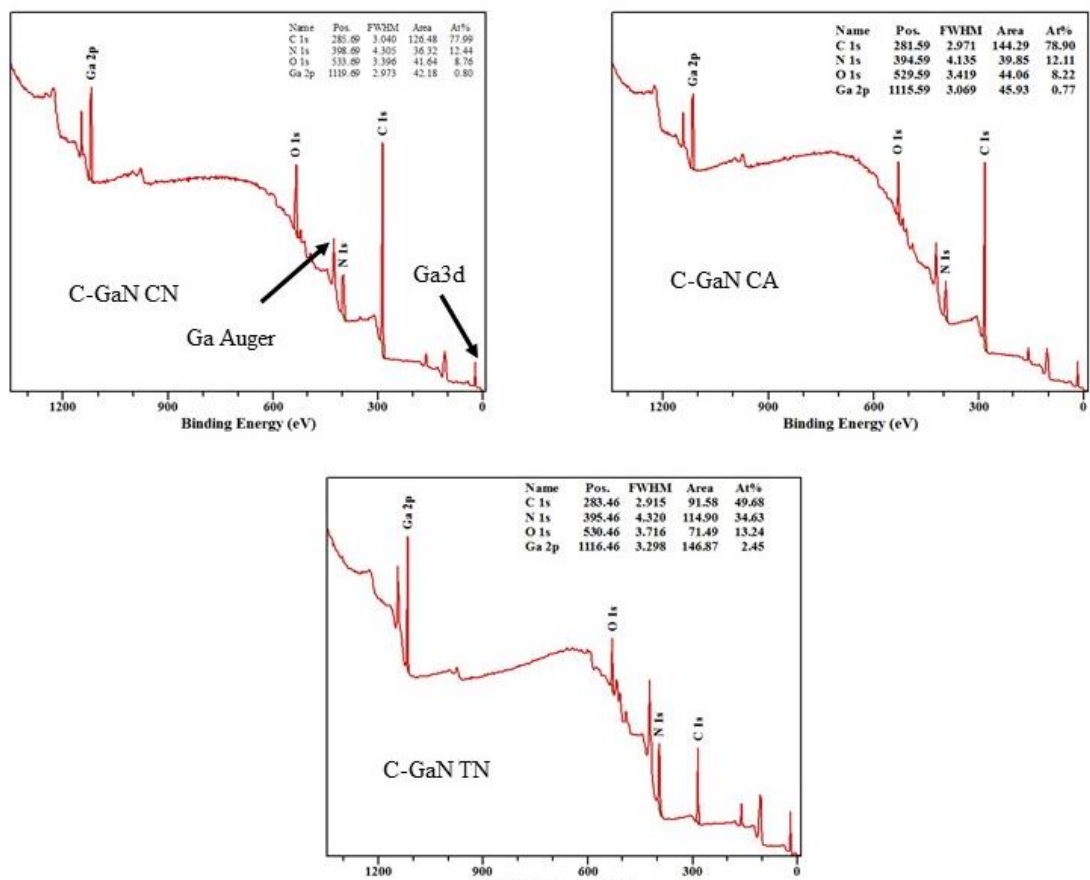


Figure 6-8: Wide-scan XPS spectra of C-GaN (C-GaN CA, C-GaN CN and C-GaN TN) samples.

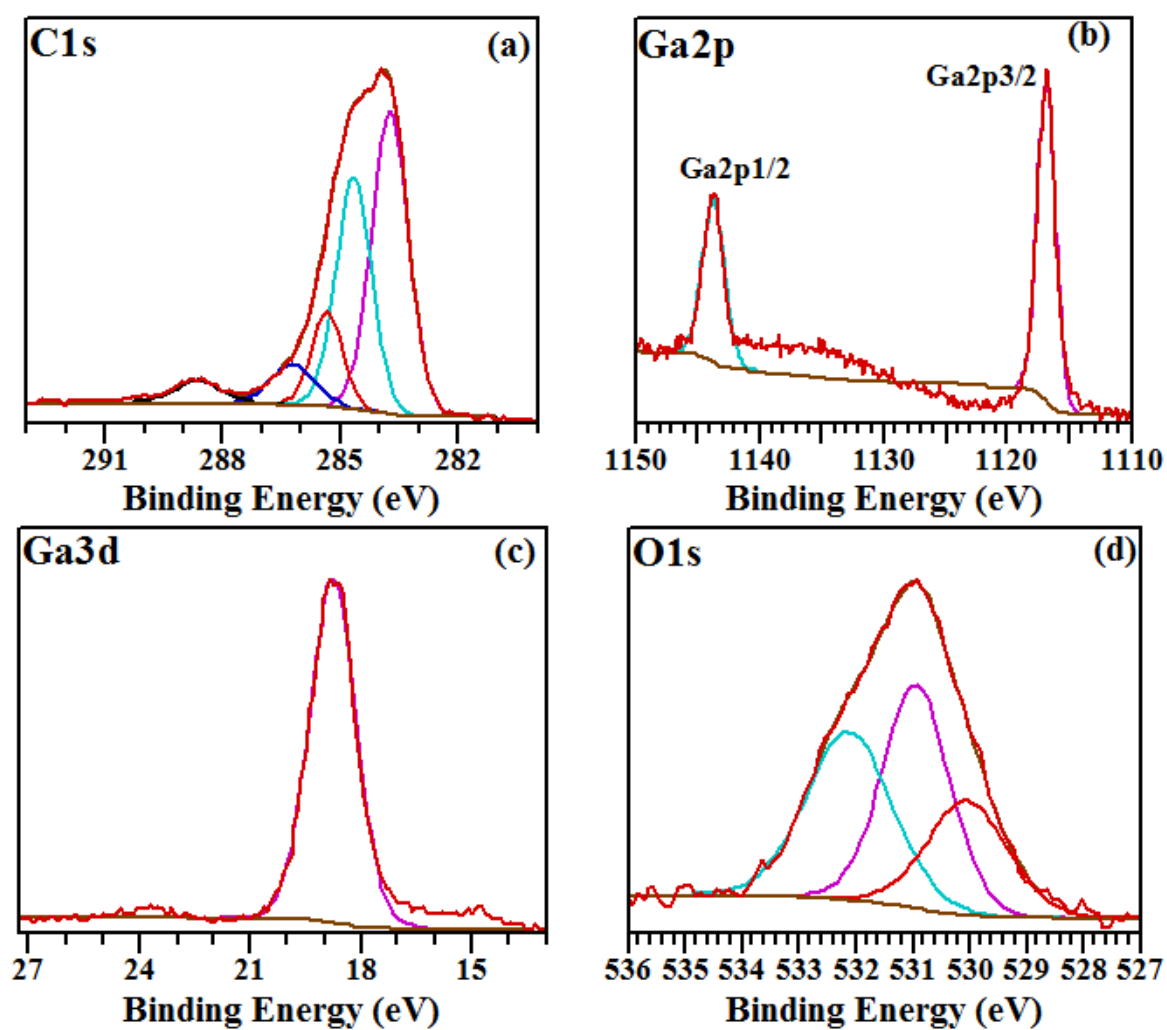


Figure 6-9: The XPS general scan and spectra of deconvoluted C1s, Ga2p, Ga3d and O1s peaks of C-GaN C1

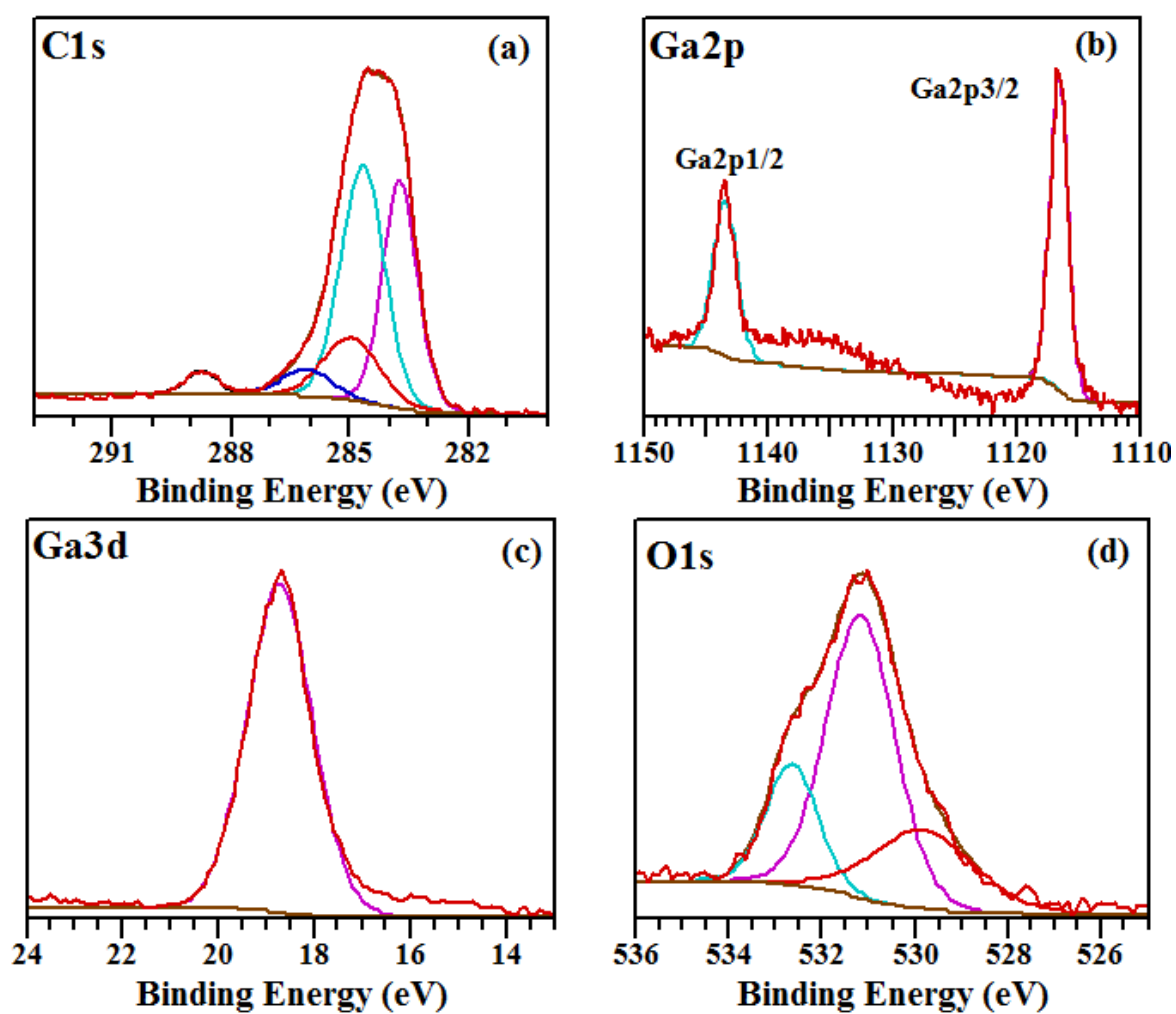


Figure 6-10: The XPS general scan and spectra of de-convoluted C1s, Ga2p, Ga3d and O1s peaks of C-GaN C2

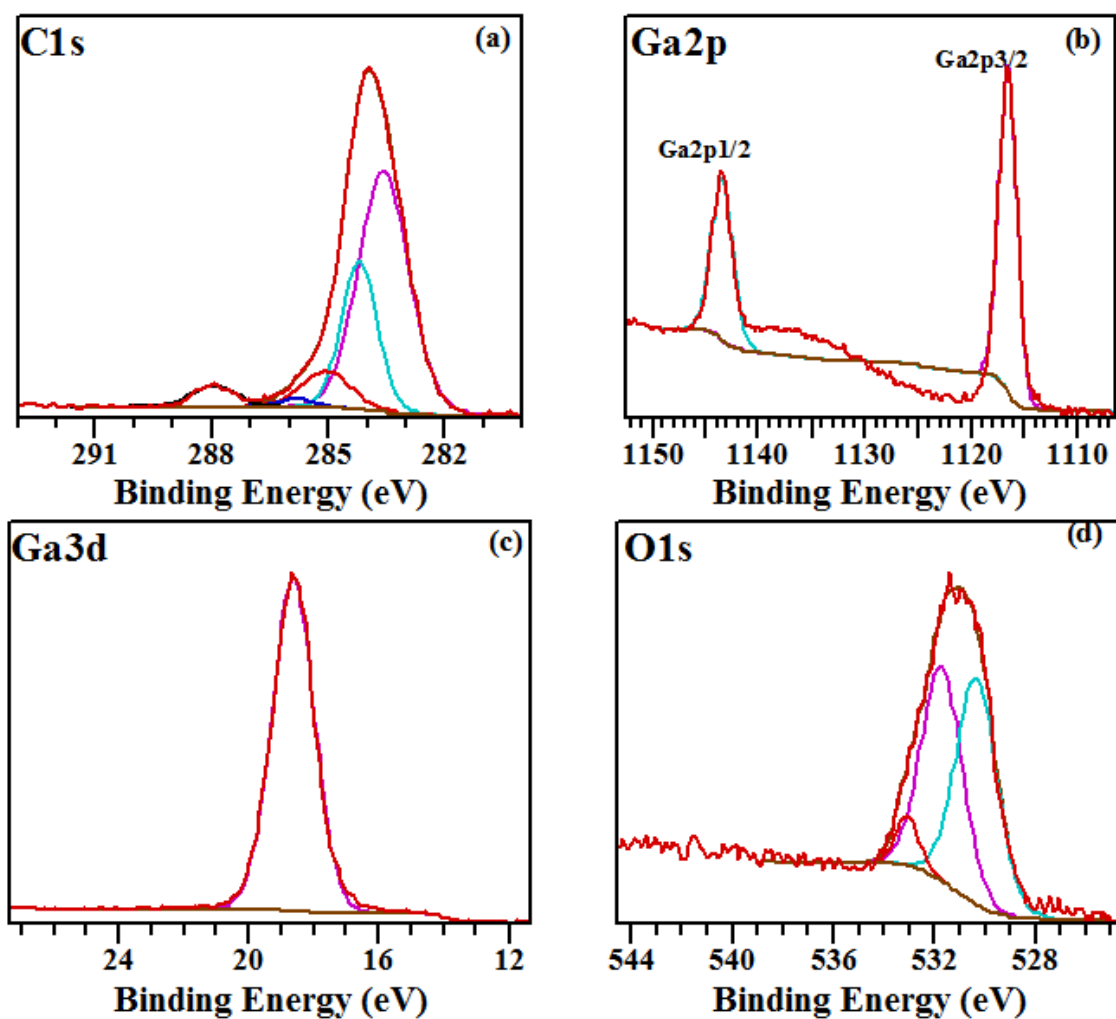


Figure 6-11: The XPS general scan and spectra of deconvoluted C1s, Ga2p, Ga3d and O1s peaks of C-GaN N8

Table 6-5: The binding energies of the carbon coated GaN samples (C-GaN)

Sample	Ga2p (eV)	N1s (eV)	O1s (eV)	C1s (eV)
C-GaN CN	1119.7	398.7	533.7	285.7
C-GaN CA	1115.6	394.6	529.6	281.6
C-GaN TN	1116.5	395.5	530.5	283.5
Pure GaN	1116.7	397.0	531.0	284.6

Table 6-6: Elemental compositions of C-GaN

Samples	C1s (at. %)	N1s (at. %)	O1s (at. %)	Ga2p (at. %)
C-GaN CN	77.99	12.44	8.76	0.80
C-GaN CA	78.90	12.11	8.22	0.77
C-GaN TN	49.68	34.63	13.24	2.45

Table 6-7: (a) Summary of fitted C1s XPS of C-GaN

Samples	sp² C-C	sp³ C-C	sp³C-N	O-C=O	O-C
C1	283.7	284.7	285.3	286.2	288.7
C2	283.7	284.7	286.0	286.1	288.8
N8	283.6	284.2	285.1	285.8	287.9

Table 6-8): Summary of fitted O1s XPS of C-GaN

Samples	O-C	O=C	C-O
C1	530.0	530.9	532.1
C2	529.8	531.2	532.6
N8	530.3	531.7	533.1

Table 6-9: Summary of fitted Ga2p and Ga3d XPS of C-GaN

Samples	Ga2p_{3/2}	Ga2p_{1/2}	Ga3d
C1	1116.9	1143.7	18.8
C2	1116.5	1143.4	18.7
N8	1116.6	1143.4	18.6

Table 6-10: % concentration of C1s of C-GaN

Samples	sp ² C-C	sp ³ C-C	sp ³ C-N	O-C=O	O-C
C1	44.30	32.67	11.58	7.01	4.45
C2	33.50	42.58	14.58	5.88	3.46
N8	58.77	25.91	9.01	1.62	4.69

Table 6-11: % concentration of O1s of C-GaN

Samples	O-C	O=C	C-O
C1	23.90	38.85	37.24
C2	23.63	57.57	18.80
N8	48.60	45.60	6.12

Table 6-12: % concentration of Ga2p and Ga3d of C-GaN

Samples	Ga2p _{3/2}	Ga2p _{1/2}	Ga3d
C1	62.45	37.55	100
C2	61.17	38.83	100
N8	63.13	36.87	100

6.3 Conclusions

GaN nanostructures has been successfully synthesized and coated with carbon. The type of carrier gas used was found to determine the amount of carbon on GaN. When Ar was used as a carrier gas more than 2.5 times carbon was deposited on GaN than with N₂ as a carrier gas. The amount of carbon deposited on the samples does not depend on the carbon source used but on the type of carrier gas and the partial pressure used.

PL spectra shows that the intensity of YL emission decreases with the deposition of carbon on the GaN surface. The intensity of the YL peaks of both samples that used argon as a carrier gas have both shifted slightly. When the carbon source C₂H₂ was used it results in the NBE peaks' photon energy shifted upwards.

XPS spectra there is high carbon contents on the surface of GaN (≈ 1.5 more) for samples that used acetylene as carbon source compared to the one that used toluene irrespective of the types of carrier gas used.

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Chapter 7: Applications of functionalized carbon nanostructures

7.1 Sensor applications of C-GaN

7.1.1 Introduction

III-V based semiconductor compounds have been widely used for sensor applications and the detection of diverse gases in standard and harsh conditions. Among these GaN remains one of the more promising compound semiconductors which are currently being used in gas sensing devices. The use of GaN nanostructures and nanowires as a gas sensor is driven by its high stability, high surface electrochemical potential and tunable electronic and physicochemical properties. Several authors have reported the use of GaN gas sensors [1], [2], [3], [4], [5], [6], [7]. Most GaN gas sensors makes use of a catalytic metal to enhance their surface reactivity [8]. GaN gas sensors have greater chemical inertness and operate under harsh environment at high temperature [9], [10]. As a gas sensor, pure GaN does not operate at room temperature as they tend to have poor sensitivity. Thus GaN based sensor properties can be enhanced through functionalization or catalytic decoration or coating with metals such as Pd, Pt, etc. [11], [2], Pt [12], [3], [7] or Au [13]. These metals enhance the GaN surface reactivity and can be used to detect gases like H₂, CO, CH₄ and NH₃ but they usually operate at high temperatures (200 – 600 °C).

GaN sensors are used for indoor fire control as well as industrial safety especially in instances for which toxic and flammable gases can be prevalent and active in low amounts or thresholds. Thus sensors for toxic as well as highly combustible gases like NH₃, CO, CH₄ and H₂ are in high demand [14]. For example hydrogen sensors are used for the detection of fuel leaks in space craft, automobiles and gas emission in industries [15], [16].

There are few reports on the use of pure GaN operating at room temperature [17], [18] for the detection of hydrogen. Indeed, there are no reports on the use of carbon coated GaN as a gas sensor. Herein we report on the use of easy to fabricate carbon-coated GaN as a gas sensor.

7.1.2 Fabrication of the C-GaN device

As-synthesised GaN nanopowders were loaded into a quartz boat and placed in the centre of a quartz tube. Pure N₂ or Ar (Afrox) was allowed to flow at a rate of 80 mL/min through the quartz tube while heating the furnace to 600 °C. When the desired temperature was reached, acetylene (C₂H₂) (Afrox) or the pure Ar gas was allowed to pass through toluene in a bubbler at the same flow rate of 80 mL/min while fixing the N₂ flow rate at 80 mL/min. After 45 minutes, the C₂H₂ was switched off and the furnace allowed cooling down to room temperature under N₂/Ar ambient. When the furnace has cooled to room temperature, the boat was removed and its content weighed to establish the amount of C-GaN formed. In all instances the same mass of C-GaN powders were used as the active layer in the sensor fabrication. The two samples were named according to the inert gas used; namely C-GaN CN (carrier gas N₂) and C-GaN TA (carrier gas Ar).

7.1.3 Measurement of the gas-sensing performance

The gas sensing response of the C-GaN device was measured using a gas sensing station KSGAS6S (KENOSISTEC, Italy). The nanoparticles were ultrasonically dispersed in ethanol and drop-coated on alumina sensing substrates. The device had a Pt electrode on the top surface and a micro-heater on the bottom surface. The sensor material was deposited on the interdigitated Pt electrode structure by drop-coating. The deposited layer was dried at 60 °C for 2 h to remove the organic solvent prior to the measurements. The sensor temperature was set at 25 and 250 °C using an applied heater voltage of 0.5 V. Various concentrations of the target gas were obtained by varying the flow rates of a mixture of target gas and dry air. The conduction or resistance response of the device to the various concentrations (5, 10, 20, 40, 60, 80 and 100 ppm) of targeted gases was measured by a Keithley 6487 picoammeter/voltage source meter. The Keithley 6487 picoammeter/voltage produced a voltage sweep while simultaneously measuring the resulting current. It also provided both sweeping and biasing. The response and recovery of the device were also measured. Figure 7.1 (top) shows the sensor device together with the respective heater and electrical contacts and Figure 7.1 (bottom) illustrates the schematic of the constituent layers of the sensor element (UST Umweltsensortechnik GmbH, Germany) similar to the one used in our measurements.

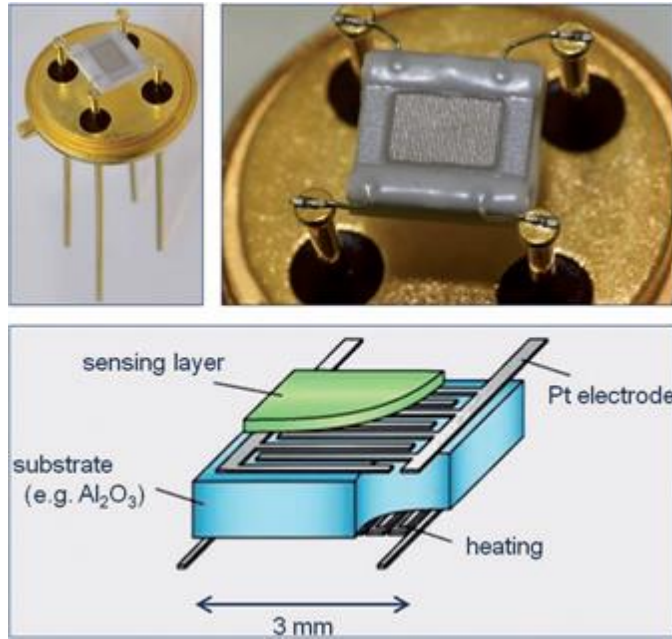


Figure 7-1: (top) the device and (bottom) an example of the sensor substrate similar to the one used in the sensing measurements [19].

The gas sensor response for carbon coated GaN (C-GaN) samples was measured in the form of a current produced by the sensor upon exposure to different target gases at operating temperatures of 25 and 250 °C. The response was realised by switching the analyte gas on for 300 seconds. The sensor recovery investigated by switching the analyte gas off for 300 seconds while simultaneously allowing synthetic air to flow through the test chamber.

The sensor sensitivity (S) is defined as shown in equation 7.1:

$$S = \left[\frac{R_{gas} - R_o}{R_o} \right] \times 10 \quad [7.1]$$

where R_{gas} is the resistance of the C-GaN that was saturated with adsorbed ambient gas during the filling half cycle and R_o is the resistance in the pumping half cycle [20].

The response and recovery time are defined as the time required for a target gas to reach 90% of the saturation value and the time required to recover 10% of the base value respectively [21], [22], [23], [24]. The recovery and response times are illustrated in Figure 7.2.

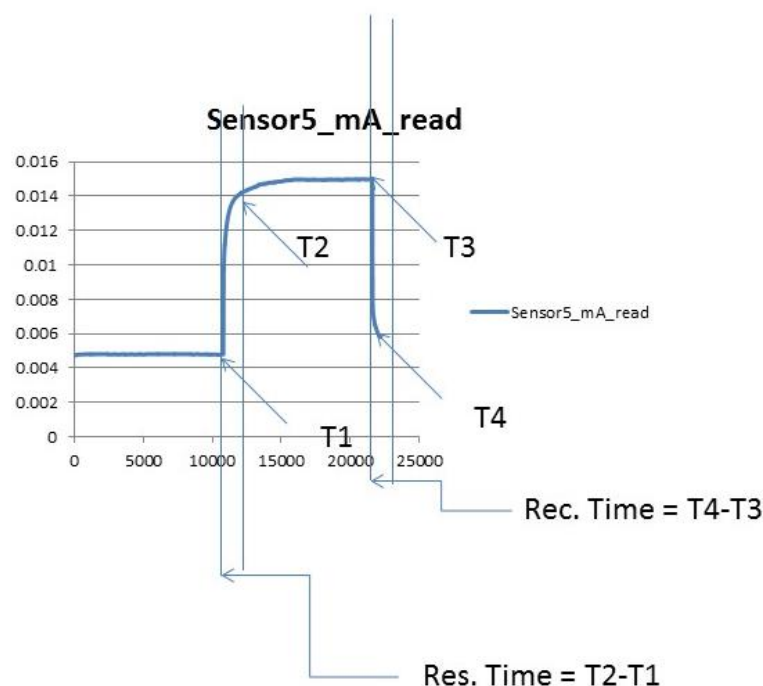


Figure 7-2: Illustration of recovery and response times

7.1.4 Results and discussion

The response of the carbon coated samples (C-GaN TA and C-GaN CN) to four gases namely H₂, CO, CH₄ and NH₃ was compared with the response of a pure GaN sensor. The pure GaN based sensor showed no response to all the analytic gases at room temperature or at 250 °C. The carbon coated GaN samples on the other hand responded at room temperature only. A good sensor should have rapid response and recovery times i.e. should respond and recover immediately to a gas that is to be detected and after the purging of the analyte gas with an inert gas.

Figures 7.3 - 7.6 show the resistance versus time graphs for the two carbon coated samples namely C-GaN TA and C-GaN CN. All the responses are for measurements at room temperature. There is no response for measurements carried out at 250 °C for the two samples. It should again be mentioned that pure GaN showed no response to all the analytic gases at room temperature or at 250 °C. Figures 7.7 to 7.10 show the sensitivity versus concentration graphs for the two samples as well as the selectivity for the different gases.

Electrical characterisation shows that when C-GaN TA is exposed to CH₄ it induces an increase in the channel resistance with increasing concentration of CH₄ (Figure 7.7). The device (C-GaN TA) shows a better sensitivity to CH₄ compared to C-GaN CN despite the poor response. This

response is attributed to the electrical charge transfer induced on the surface of the GaN probably aided by the carbon atoms (electron donor or acceptor). The sensitivity could be due to the surface charge created by the carbon on the surface of the GaN. However, it has a poor response after the concentration increased beyond 20 ppm. In Figures 7.8, 7.9 and 7.10, the device C-GaN TA showed a better sensitivity to NH_3 , CO and H_2 respectively compared to the device C-GaN CN. These results depend on the interactions of the different gaseous species with GaN, C-GaN CN and C-GaN TA. The difference between the two samples relates to the different amounts of carbon (CN ~ 3.9% and TA ~ 9.9% of carbon). This shows that the presence of more carbon on the surface favours the chemical interaction between the devices with the gas molecules. TGA results shows that the device C-GaN has more carbon coated or deposited on the surface of GaN. As observed in Figures 7.8, 7.9 and 7.10 the sensitivity of H_2 increases with the gas concentration beyond 80 ppm for the device C-GaN TA whereas the concentration drops after 80 ppm for NH_3 and 40 ppm for CO.

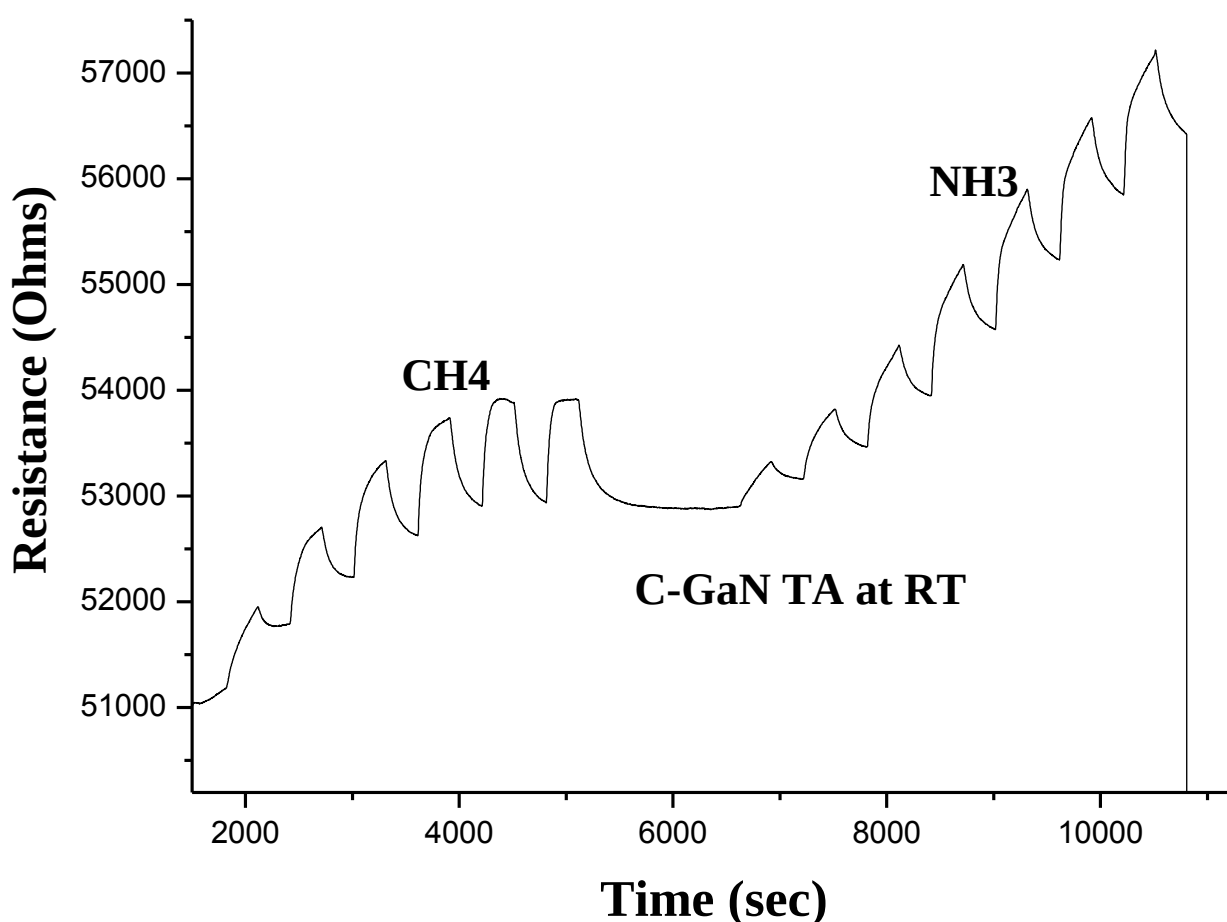


Figure 7-3: Resistance vs time graph for CH_4 and NH_3 at room temperature (C-GaN TA)

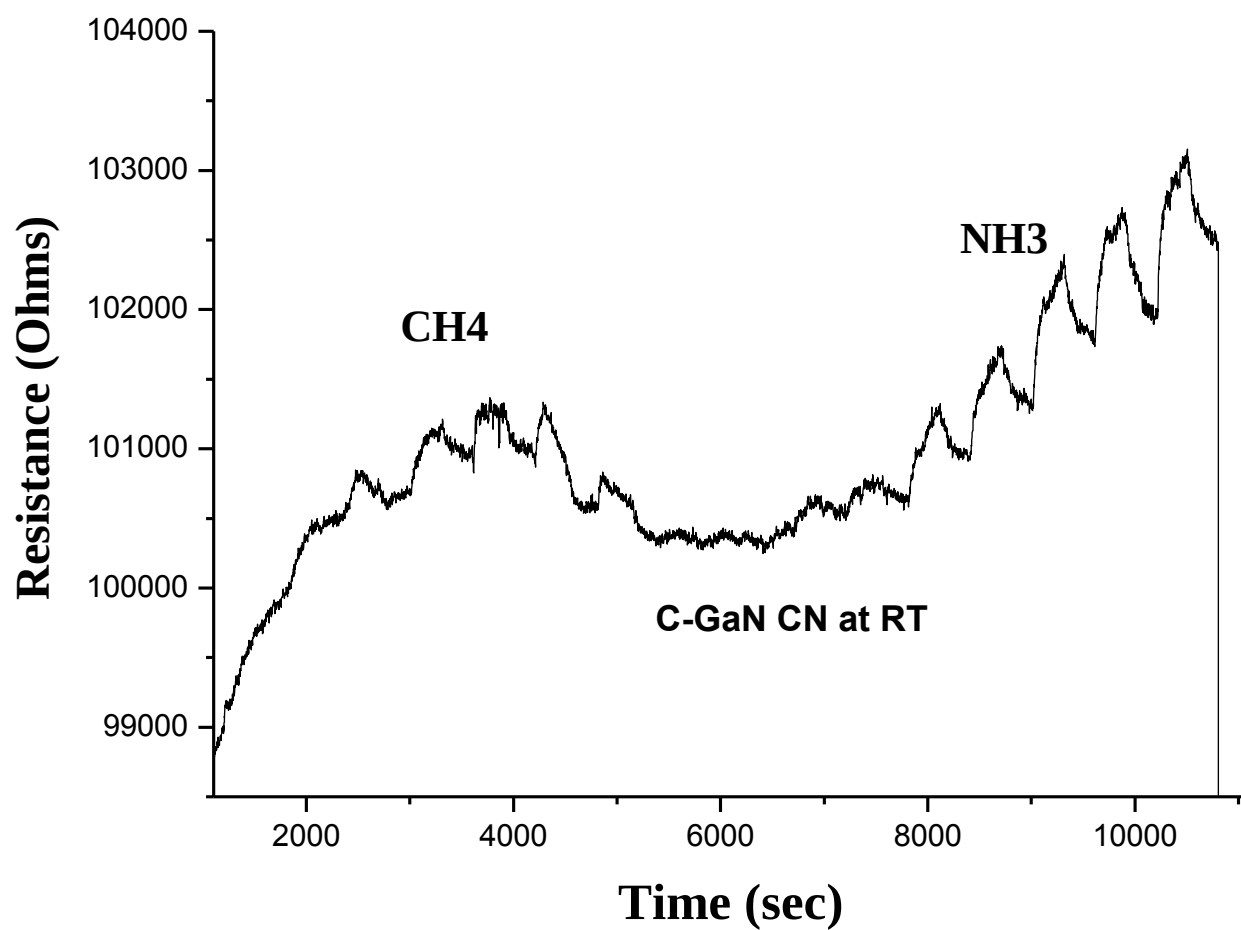


Figure 7-4: Resistance vs time graph for CH₄ and NH₃ at room temperature (C-GaN CN)

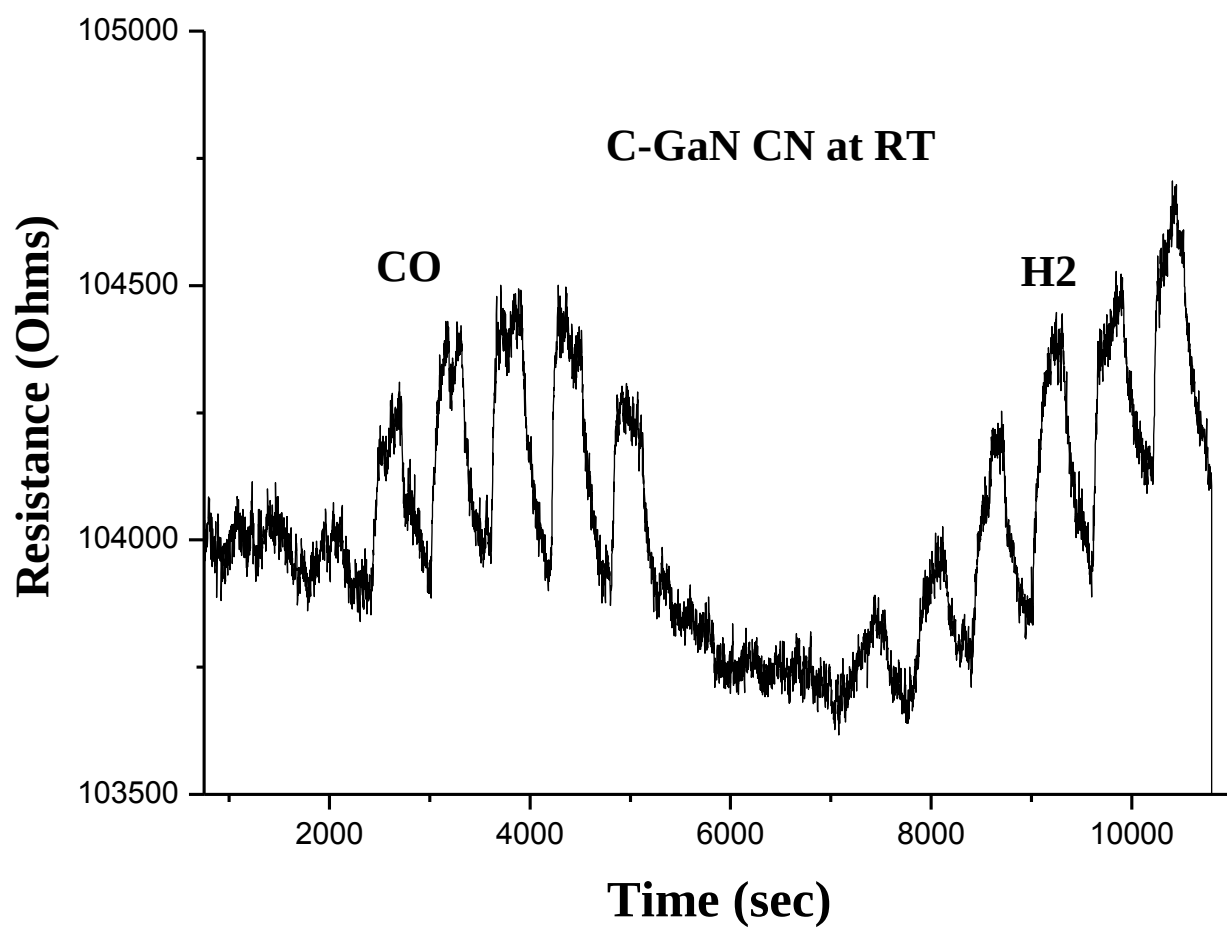


Figure 7-5: Resistance vs time graph for CO and H₂ at room temperature (C-GaN CN)

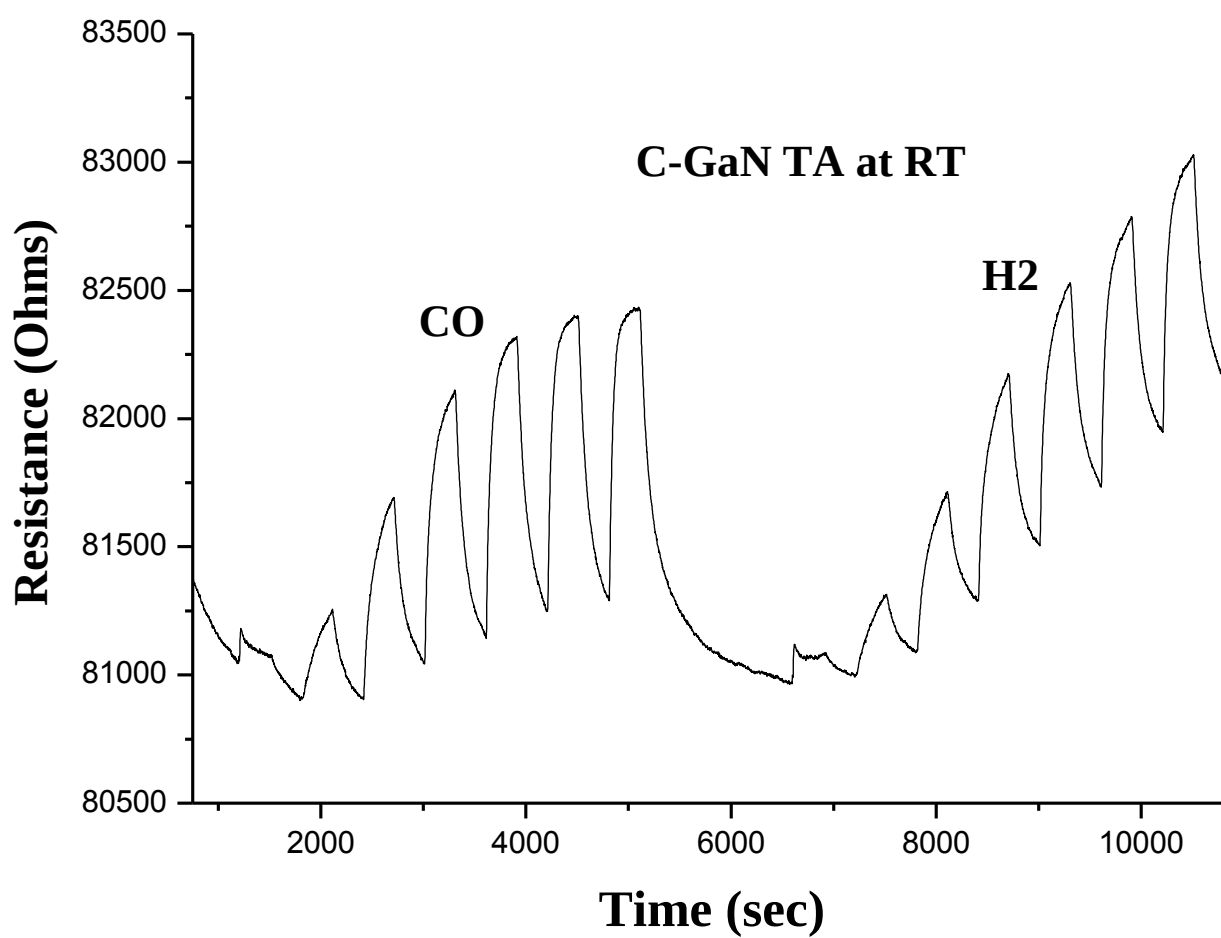


Figure 7-6: Resistance vs time graph for CO and H₂ at room temperature (C-GaN TA)

The sensor and recovery times for the two sample are shown in Table 7.1. The response time ranged from 178 – 291 sec while the recovery time ranged from 236 – 296 sec. For the sample C-GaN TA the sensitivity increase is constant from 5 to 40 ppm for the three gases with the exception of ammonia.

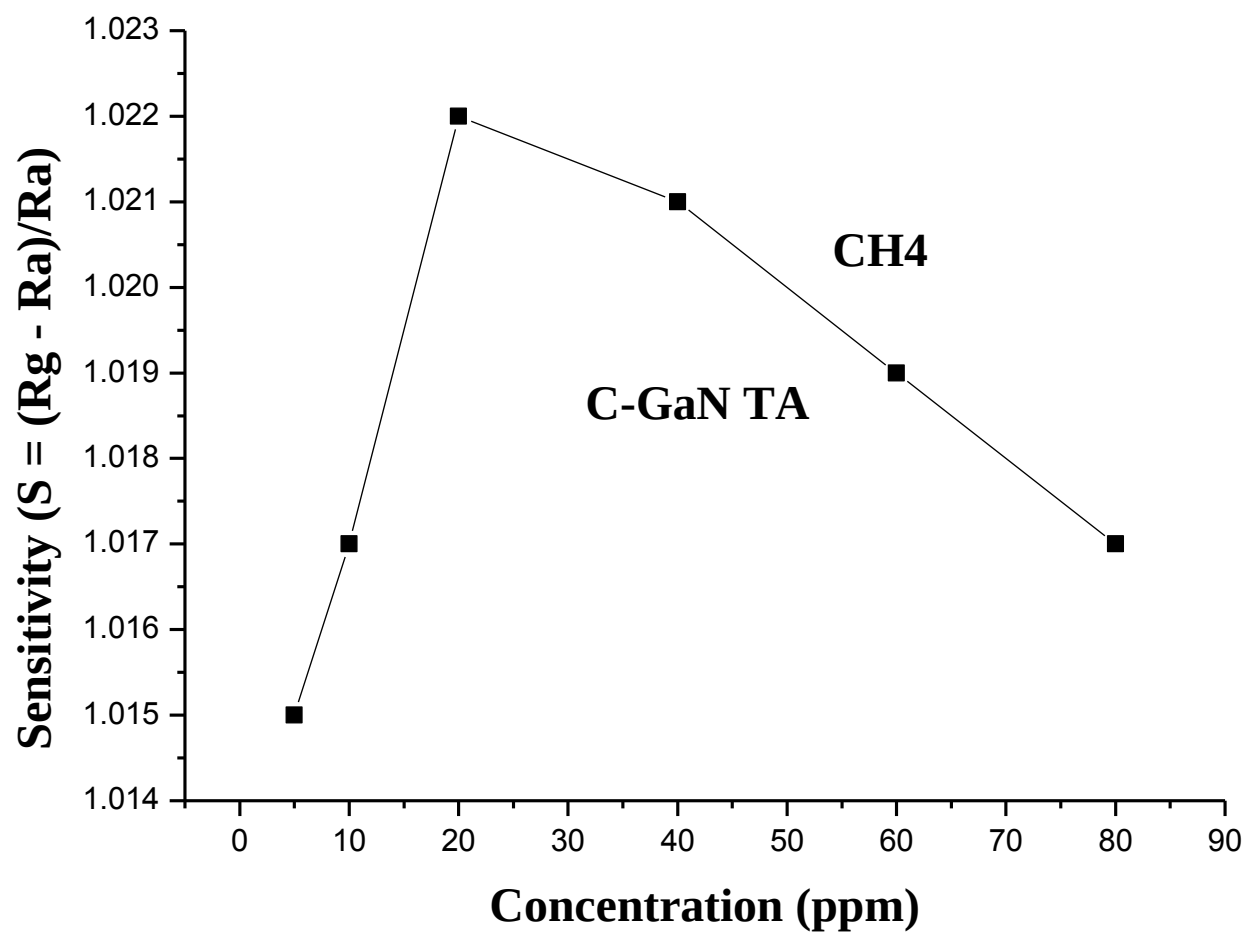


Figure 7-7: Sensitivity for CH₄ at room temperature using C-GaN TA

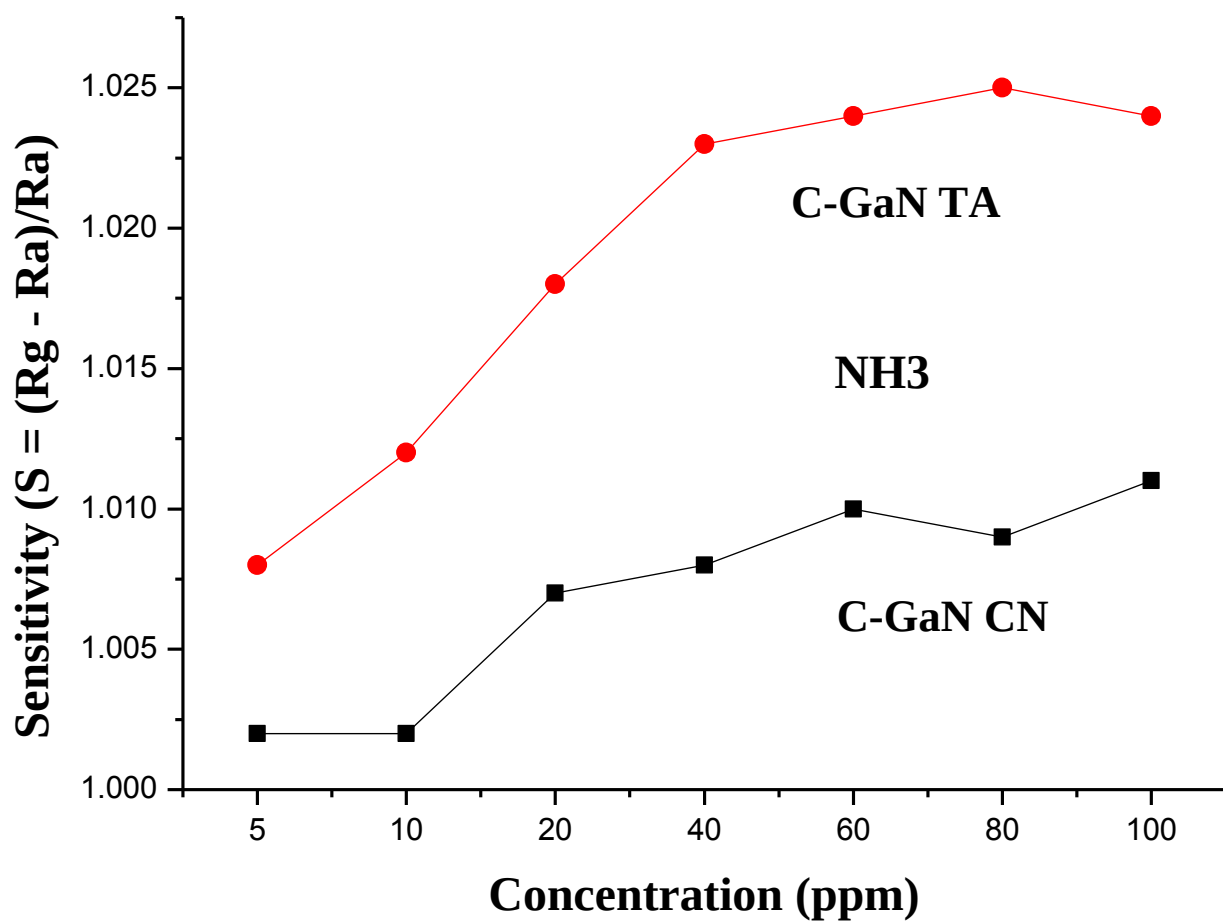


Figure 7-8: Sensitivity of NH_3 at room temperature for C-GaN CN and C-GaN TA

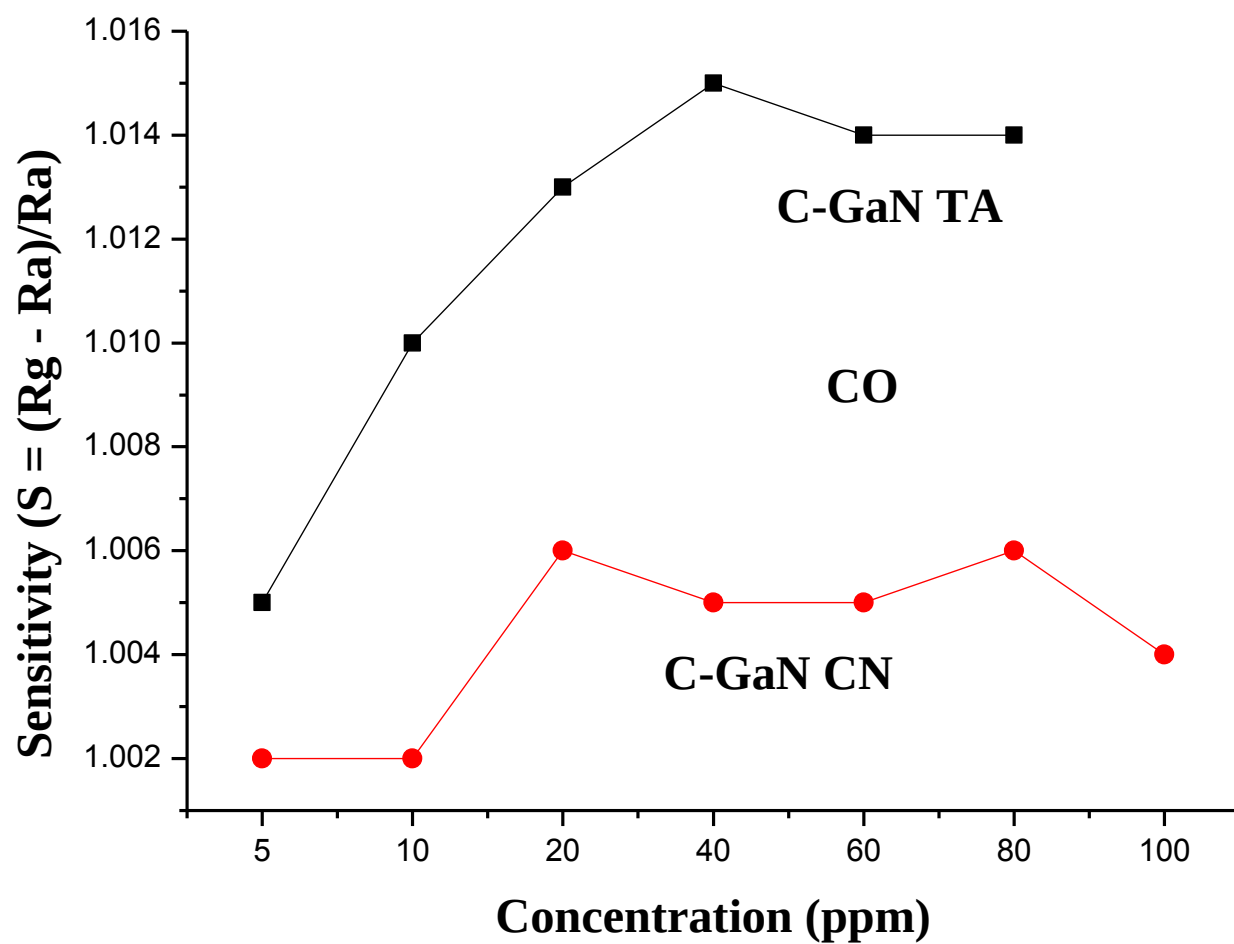


Figure 7-9: Sensitivity of CO at room temperature for C-GaN CN and C-GaN TA

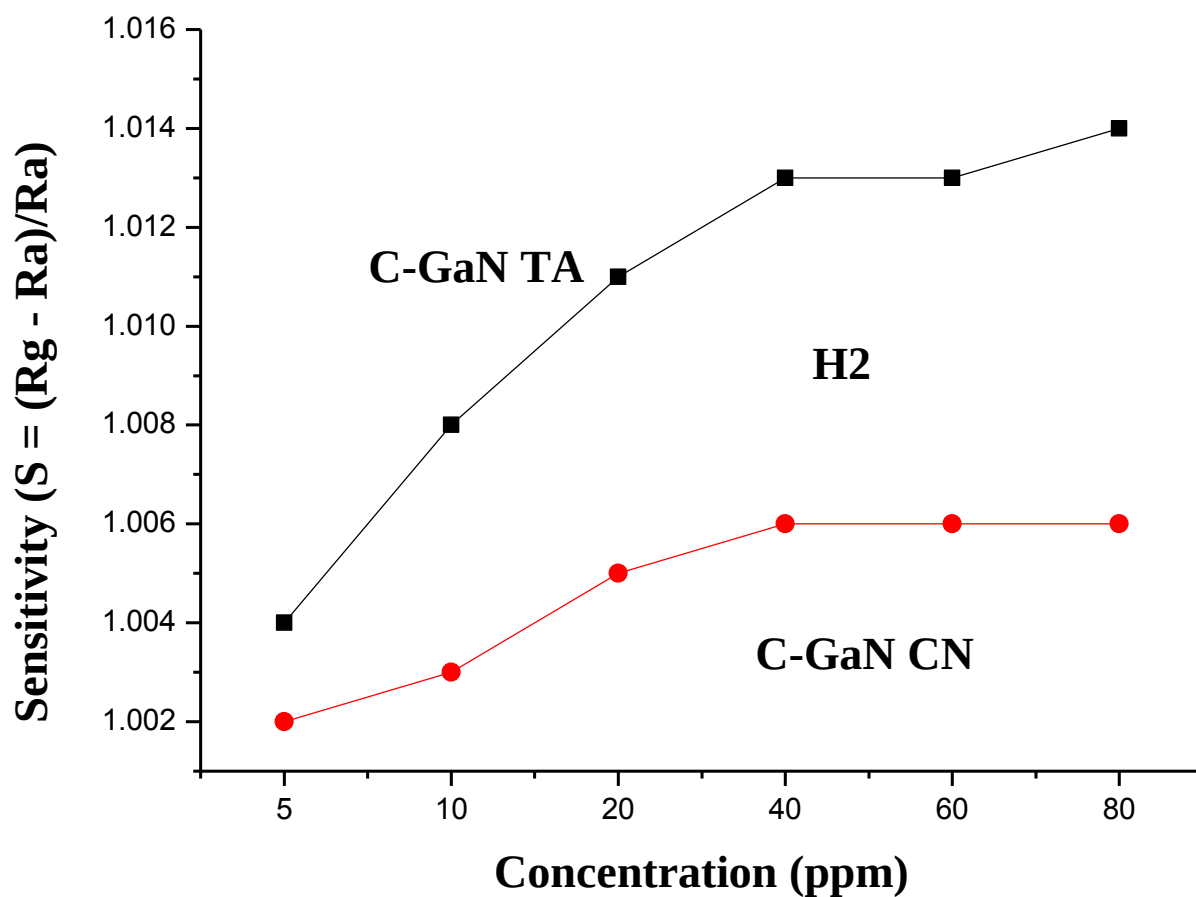


Figure 7-10: Sensitivity of H₂ at room temperature for C-GaN CN and C-GaN TA

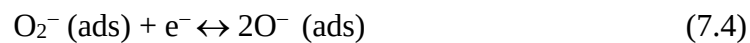
The response and recovery times for the carbon coated samples (C-GaN TA and C-GaN CN) measured at room temperature are indicated in Table 7.1.

Table 7-1: Recovery and response times for C-GaN samples measured at room temperature.

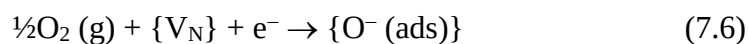
Sample	Gas type (analyte)	Response time (s)	Recovery time (s)
C-GaN TA	CO	256	294
C-GaN CN	CO	205	296
C-GaN TA	H ₂	291	293
C-GaN CN	H ₂	222	240
C-GaN TA	CH ₄	178	281
C-GaN CN	CH ₄	198	236
C-GaN TA	NH ₃	230	283
C-GaN CN	NH ₃	253	290

7.1.5 Mechanism of gas adsorption on C-GaN sensor device

Reports in the literature [25], [5], [17] show that the sensing of reducing gases by an n-type semiconductor involves a mechanism based on the change in electrical resistance of the sensor by an adsorption-desorption mechanism of gas molecules on the surface of sensing materials. For Group III nitride semiconductor based sensing materials [5], [17], N vacancies have been proposed to act as the sorption sites for gas molecules. Lee and co-workers [26] demonstrated that oxygen is adsorbed at these vacancies. Thus, oxygen sorption plays a significant role in the electrical properties of GaN materials. When GaN based gas sensors are exposed to air, oxygen molecules in the air are firstly adsorbed on the surface, and these surface-adsorbed molecules undergo chemisorption to form oxygen species (O_2^- , O^- and O^{2-}) [27] via capture of electrons from the GaN conduction band and this mechanisms is temperature dependent. Thus, the resistance of the sensor increases owing to a decrease in the carrier concentration with the formation of a depletion zone within the surface. Tonzzer and co-workers [28] reported that the chemisorbed oxygen species depend strongly on the temperature. The O_2^- molecule is generally chemisorbed at low temperatures (below 100 °C), whereas when the temperature > 100 °C, then O^- and O^{2-} atomic species are preferentially chemisorbed. Thus the O_2^- species vanish with increasing temperature [17]. The different reactions can be summarised as shown below [26], [29], [30], [31];



Each of the samples has the starting species (O^-) are free from metal for the testing of the four different gases, the sensing activity can only take place at the surface of the sample. The sensing mechanism involves the various gases being adsorbed at the surface of the material, where they are induced to change an electrical resistance of the surface. Since there are defects site on the surface of the carbon coated GaN, the change in resistance could only be achieved by physisorption at these defective sites. Chitara and co-workers reported that these defects are likely to be N vacancies in GaN which can act as sorption sites for gas molecules on the surface [17]. When oxygen is adsorbed at the nitrogen vacancies (V_N) in n-type GaN, the following reaction is expected to take place [32].



The gases are detected by measuring the resistance changes [33].

7.1.6 Conclusions

We have demonstrated for the first time use of carbon coated GaN as a sensor at room temperature and studied the sensor response to four gases (CO, H₂, NH₃ and CH₄) at low ppm. The sensitivity of the device is proposed to be related to defects on the surface of the carbon coated GaN. Sensor measurements show that the carbon coated device, C-GaN TA, has a better sensitivity compared to C-GaN CN at room temperature. The response and recovery times are reasonable but no attempt at optimization has yet been undertaken.

7.2 Transition metal oxide decorated N-CNTs for sensor applications

7.2.1 Introduction

Metal oxides (e.g SnO₂) have much higher thermal and temporal stability hence their use in gas sensors [34]. Metal oxide sensors work on the principle of chemiresistance viz. the change in electrical conductivity or resistivity of the material on exposure to a target gas. Gas molecules interacting with metal oxides either act as a donor or acceptor of charge carriers. The contribution of charges to the oxide therefore alters its conductivity. The increase or decrease of resistance of metal oxide depends upon its majority carriers and the nature of the gas molecules (whether oxidizing or reducing) in ambient condition. For n-type materials, oxidizing gases such as CO₂, NO₂ (acceptor) increase the resistance of the metal oxide material while, reducing gases CO, NH₃, H₂ (donor) decrease the resistance of p-type materials (G.F. Fine et al., Sensors 10 (2010) 5469). It has been reported that the CNTs are very sensitive to surrounding environment. The presence of O₂, NH₃, NO₂ gases and many other molecules can either donate or accept electrons, resulting in an alteration of the overall conductivity [35], [36]. Such properties make CNTs ideal for nanoscale gas-sensing materials, and CNTs field effect transistors and conductive-based devices have already been demonstrated as gas sensors [37], [38], [39]. However, the CNTs still have certain limitations for gas sensor application such as long recovery time, detection of limited gases,

and strong influence of humidity and other gases. Recently, the combinations of metal oxides such as SiO_2 , TiO_2 , SnO_2 , and CNTs have been received intensive research interest for various applications such as photocatalytic, anode materials for lithium-ion batteries and gas sensors [40], [41], [42]. However, their gas-sensing performance has not yet been much improved in comparison to SnO_2 as well as CNTs-based sensors. Furthermore, currently reported composite sensors still operate at elevated temperatures. To the best of our knowledge no work has been reported on N-CNT decorated SnO_2 . Reducing gases act as electron donors when interacting with metal oxide surface. During this interaction, reducing gases desorb or remove the chemisorbed oxygen ions and physisorbed hydroxyl ions from the metal oxide surface. The variation in the resistance of the material is used to detect the concentration of reducing gases by the chemical changes following REDOX reaction [43].

7.2.2 Sensor characteristics of SnO_2 and CuO decorated N-CNTs

The loading of decorated SnO_2 on the N-CNT (N-CNT-SnO_2) was determined to 5%. These nanostructured materials were subsequently ultrasonically dispersed in ethanol and drop-cast on alumina substrates equipped with a Pt interdigitated electrode on the top surface and micro-heater at the bottom. The deposited layer was dried at 60 °C for 2h to remove the organic solvent. The measurements were carried out at RT and 250 °C using NH_3 , CO and H_2 as the target gases. The concentrations of the target gas were obtained by varying the flow rates of target gas and dry air. The conduction or resistance response of the device to the various concentrations (5, 10, 20, 40, 60, 80 and 100 ppm) of targeted gases was measured by a Keithley 6487 picoammeter/voltage source meter. Figure 7.11 shows the response of SnO_2 decorated N-CNTs at 250 °C

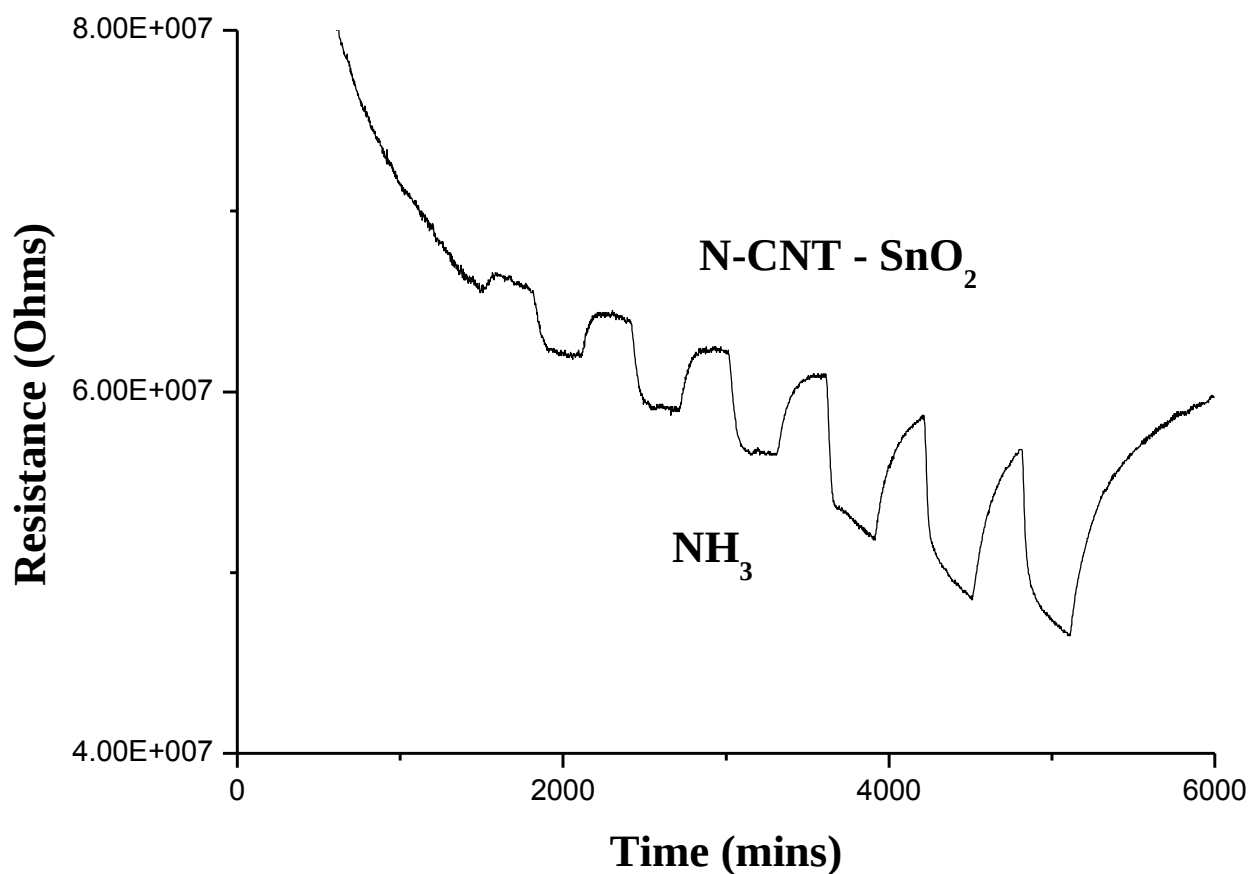


Figure 7-11: Resistance against time for NH₃ using N-CNT_SnO₂ at 250 °C

Figure 7.12 shows the sensitivities of all the gases measured for N-CNT_SnO₂ at 250 °C. All the gases respond to N-CNT_SnO₂ only at 250 °C, However, NH₃ has a better sensitivity compared to CO and H₂. The sensitivity increased up to 100 ppm, while H₂ increases up to 80 ppm then start to decrease and for CO it increases up to 40 ppm and the decreases beyond that.

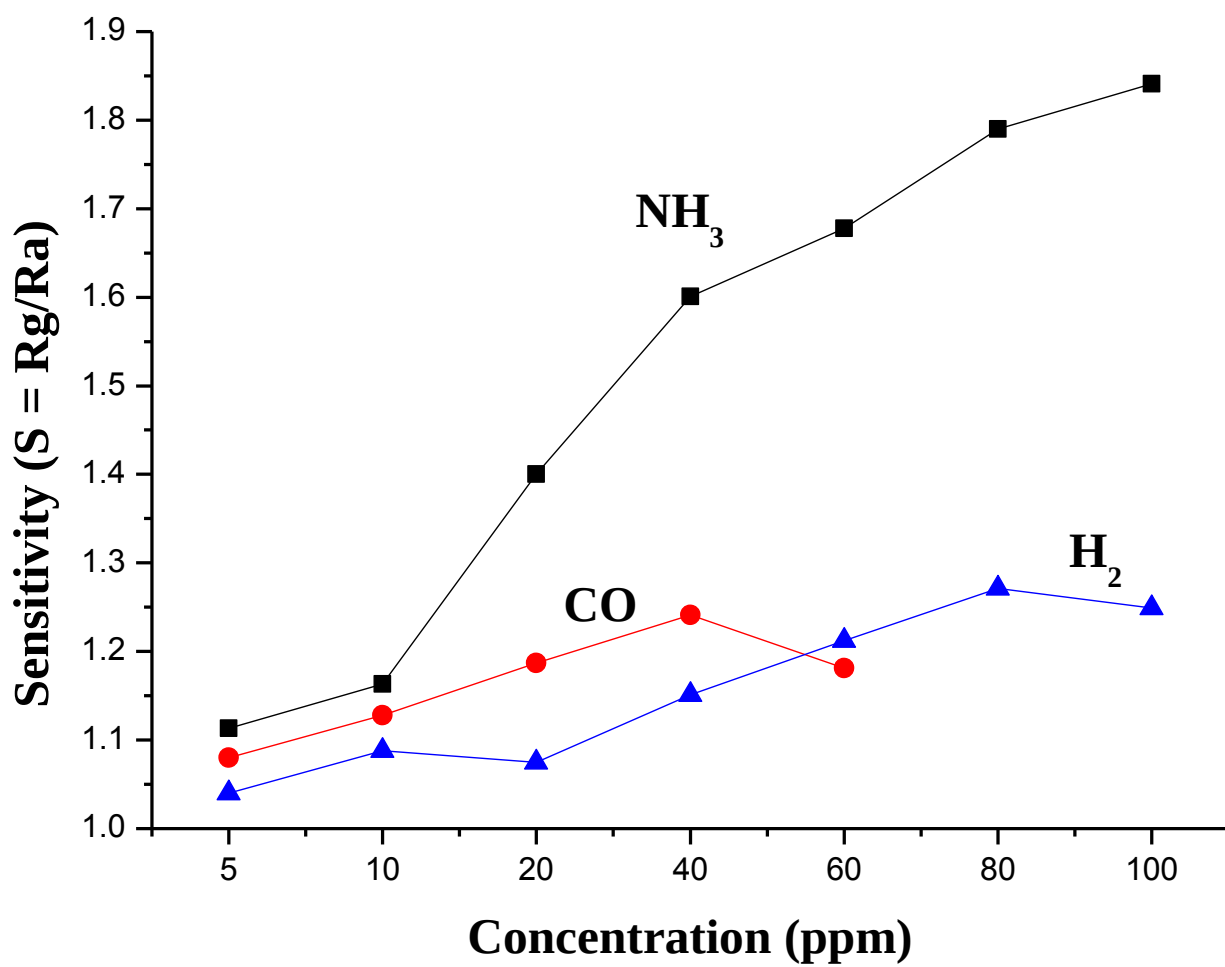


Figure 7-12: Sensitivity for NH_3 , CO and H_2 gases at 250 °C using N-CNT- SnO_2

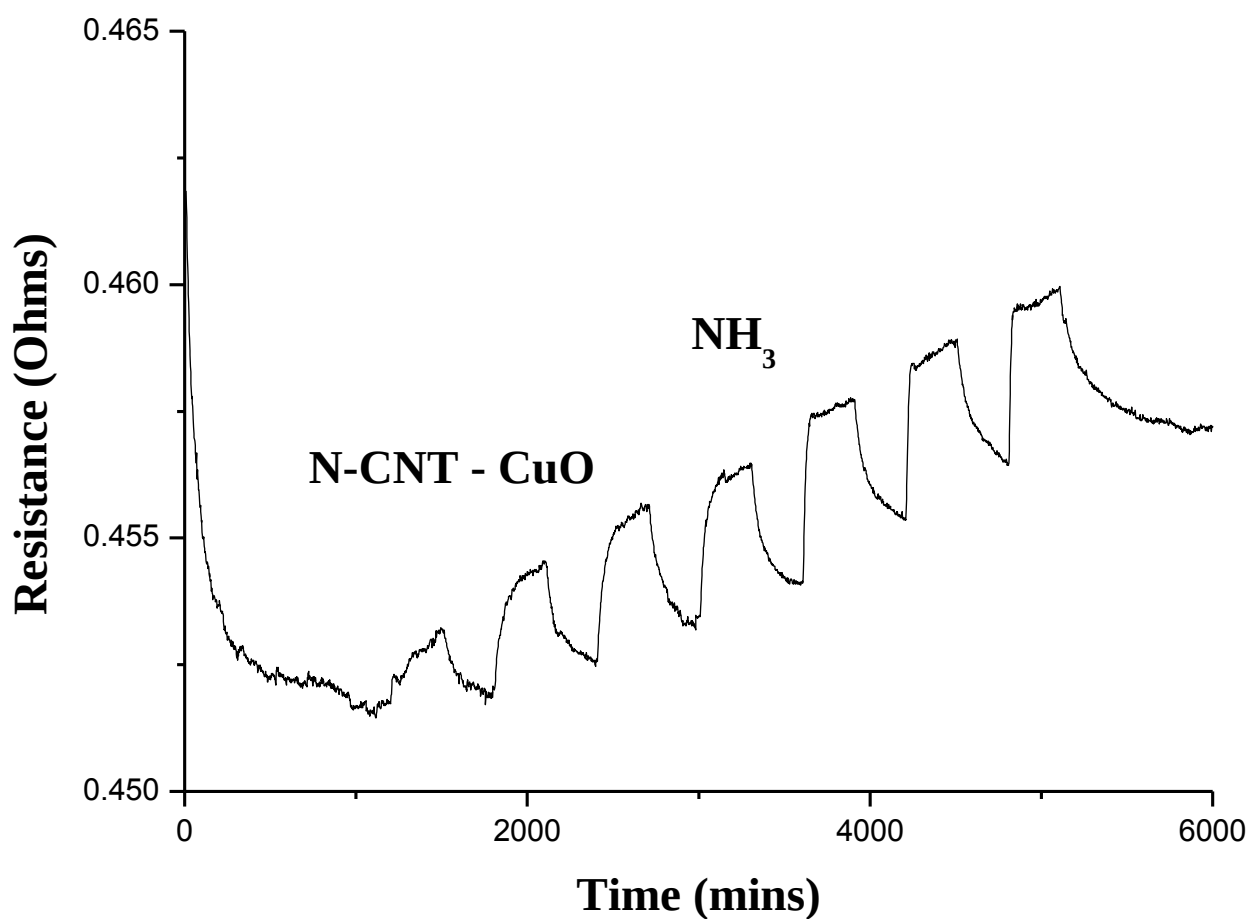


Figure 7-13: Resistance vs Time for NH_3 using N-CNT_CuO at 250 °C

Figures 7.13 shows the resistance - time graphs for N-CNT_CuO for NH_3 gas only at 250 °C. The resistance for N-CNT_CuO are very low compared to that of N-CNT_SnO₂. The low sensitivity of NH_3 for N-CNT_CuO is attributed to the low response 250 °C and not at room temperature.

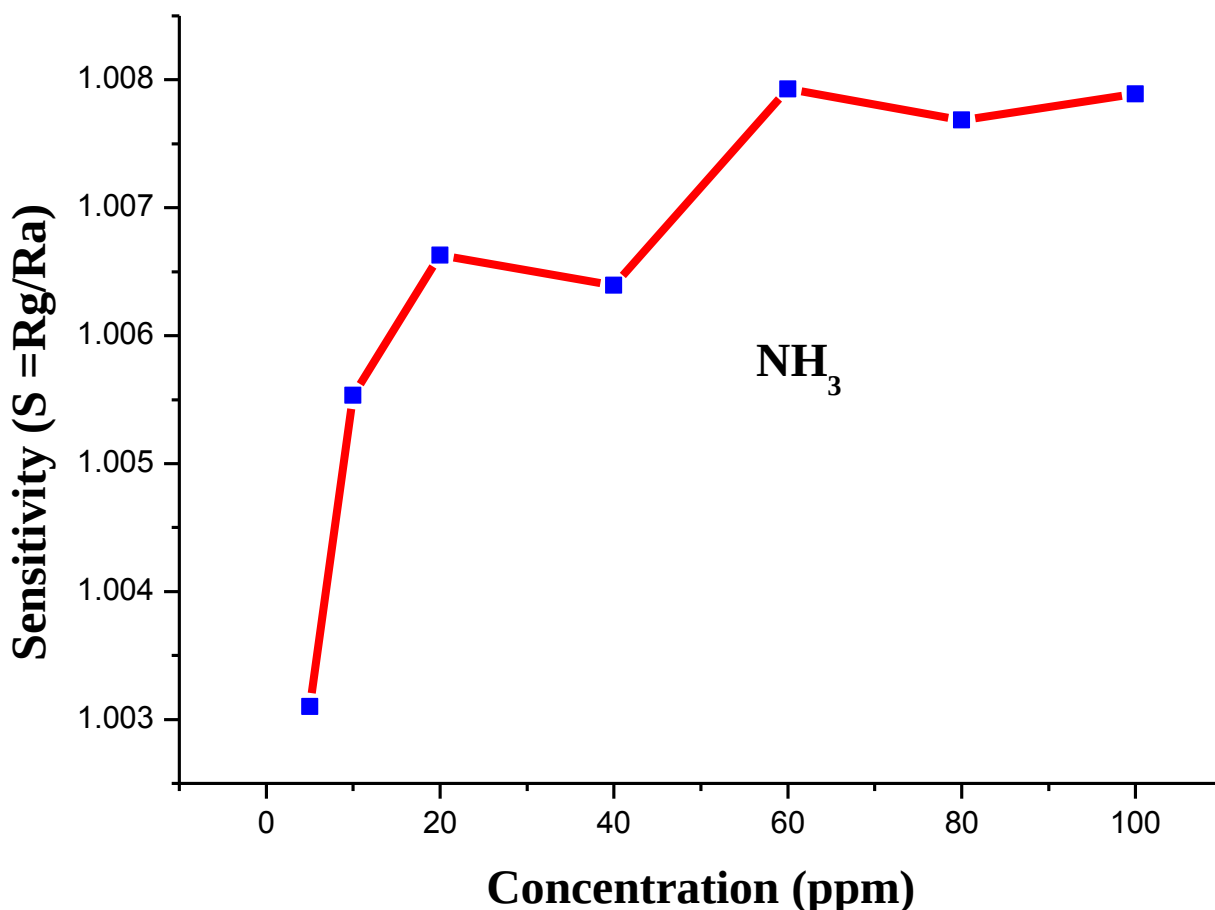


Figure 7-14: Sensitivity for NH_3 using N-CNT_CuO at 250 °C

The response is better at low concentration (up to 20 ppm) and then it saturates at about 60 ppm. Not much work has been carried out using CNT_CuO for sensing [44]. No work has been reported on N-CNT_CuO to the best of our knowledge.

7.3 Solar cells application

7.3.1 Introduction

Recently, solar cells based on soluble conjugated polymers have attracted attention because conjugated polymers are promising materials for the development of low-cost optoelectronic devices [45], [46]. Organic photovoltaic cells using conjugated polymer/fullerene blends in a bulk heterojunction architecture have been reported with efficiencies up to 6.5% [47]. A bulk heterojunction is usually composed of two interconnected network of donor and acceptor phases

in the photoactive layer e.g. fullerenes or nanocrystals for the acceptor phase and polymers for the donor phase. In a bulk heterojunction, the large interfacial area between the donor and acceptor phases provides sufficient charge separation, which is a prerequisite for solar-cell operation [48]. One of the advantages of organic semiconductors is that they can be processed in solution and layers can be deposited easily by spinning, casting, printing etc. [49], [50]. Thus, the cost of solar cell processing is reduced considerably if carbon are used. The disadvantage is that the organic semiconductors have very low charge carrier mobility because of their amorphous or semi crystalline structure [51], [52]. The diffusion length of photogenerated carriers is very short in inorganic solar cell because of poor mobility, hence the conventional p-n junction has very limited efficiency for photovoltaic conversion [53]. This drawback of organic semiconductors has been overcome with different solar cell configurations in which the p-n interface area has been increased. The typical configuration consists of a blend of a p-type organic semiconductor such as P3HT (poly(3-hexylthiophene)) and an n-type one such as PCBM (phenyl-C61-butyric acid methyl ester) [54], [55]. In a proper blend, the interface area is maximized and each semiconductor must be connected to the respective contact to provide the electrical pathway to the photogenerated electrons and holes, after they are separated at the p-n interface. Another approach is to combine them with inorganic semiconductors in organic-inorganic hybrid solar cells [56], [57]. One of the simplest configurations reported is the system of semiconductor nanoparticles with n-type conductivity such as CdS embedded in a polymeric matrix with p-type conductivity such as P3HT [58], [57]. The inorganic-organic CdS-n/P3HT-p thin film solar cell has attracted some attention because of the simplicity of depositing the absorbent P3HT layer and the excellent properties of CdS as a window layer for absorbing. P3HT is a polymeric, semi-crystalline, p-type conductor, which can easily be deposited in solution and has been used in electronic devices such as solar cells and thin film transistors [59], [60], [61].

CdS nanostructures have attracted considerable interest because of their good electron acceptor and high mobility characteristics [62]. In addition, the 2.4 eV direct band gap makes it more appropriate to be applied in organic-inorganic hybrid photovoltaic devices [63], [64], [65]. However, the morphology of hybrid cells are strongly influenced by thermal annealing because this process is able to change the interaction between the P3HT polymer and the nanoparticles and thus affect the exciton dissociation, charge transport, and overall compromise the device performance [66], [67].

7.3.2 Fabrication and device measurements

Indium tin oxide (ITO) coated glass (Merck; resistivity = $10 \Omega/\text{cm}$) was used as the substrate. The devices were fabricated on etched indium tin oxide (ITO)-coated substrates. The ITO coated glass was cleaned in an ultrasonic bath containing distilled water-acetone-ethanol solutions and the residual solvent was removed by a stream of nitrogen gas. A hole transporting layer, PEDOT:PSS was then spin coated onto the ITO coated glass substrate at 2000 rpm at 60°C for 10 mins. The resulting film was dried on a hot plate at 100°C for 15 minutes to remove any residual water. An amount of CdS nanoparticles material (5, 10, 15 and 20 mg) was dissolved/mixed with 10 mg of P3HT (Sigma Aldrich 90%, regioregular) and 1 ml of chlorobenzene. The solution mixture containing CdS, P3HT (P3HT:CdS) and the chlorobenzene were magnetically stirred for 3 hours at 60°C on a hot plate and was used without filtration. The P3HT:CdS layers (200 nm) (with the following ratios of P3HT:CdS 0.5:1, 1:1, 1.5:1 and 2:1) were spin-coated in solution at 2000 rpm and annealed at 50°C for 10 minutes. The metallization of the device was performed by thermal evaporation of aluminum (100 nm) in vacuum at 10^{-5} mbar. The power conversion efficiency determination was carried subsequently under AM1.5G conditions ($100 \text{ mW}/\text{cm}^2$) from J-V characteristics. In all the experiments OPV devices of cross-sectional area $7 \pm 1 \text{ mm}^2$ were used.

7.3.3 Characterisation

Optical absorption measurements of the film blends were made using a Cary 500 UV–visible spectrometer. A Horiba LabRAM HR Raman spectrometer equipped with an Ar ion laser (514.5 nm) was used to evaluate the structure of the active layer after the blending process. The laser power of 0.4mW was used for the Raman measurements. Photoluminescence measurements to establish the nature of the electron transfer were performed using a Horiba LabRAM HR spectrometer at an excitation wavelength of 458 nm and at room temperature. The current density–voltage (J–V) characteristics were obtained using a HP 4141B source measure unit under $100 \text{ mW}/\text{cm}^2$ illumination (AM 1.5G) generated with a Newport xenon-lamp solar simulator. All the measurements were carried out at room temperature under standard conditions.

7.3.4 Results and discussion

7.3.4.1 Optical properties of as deposited and annealed P3HT–CdS BHJ

The absorption spectra of P3HT:CdS films were recorded (a) before and (b) after heat annealing at 70 °C for 10 minutes this was to enhance the interfacial area of the CdS. Figure 7.15 shows the effect of heat treatment on the absorption spectra of P3HT:CdS films spin coated onto the ITO coated glass substrates for the as deposited (K1, K2, K3 and K4) and annealed (C1, C2, C3 and C4) at 70 °C polymer CdS hybrid blends. In all the film blends, prominent absorption features appear at 560 and 610 nm. After annealing the shoulder peak at 610 nm became more distinguishable, this is attributed to a strong interchain (π - π^*) interaction between P3HT molecules [68]. This implies that the annealing treatment improves the ordering of P3HT chains in the blend matrix. The intensity of the absorbance in each of the samples increased with thermal annealing (Figure 7.15(b)). The optical density of a thin film is the product of its absorption coefficient and the film thickness. The film thickness should stay the same after thermal annealing at temperatures below the materials melting point. Hence the increase of the absorbance in thermally annealed P3HT samples is attributed to the increase in the optical constants, that originated from the enlarged density of permitted electron levels in more crystalline P3HT samples [69]. The results highlighted the fact that the pre-metal contact thermal treatment at high temperatures increases the radiation absorption of the polymer films, which should favour the creation of excitons and thus the cell performance.

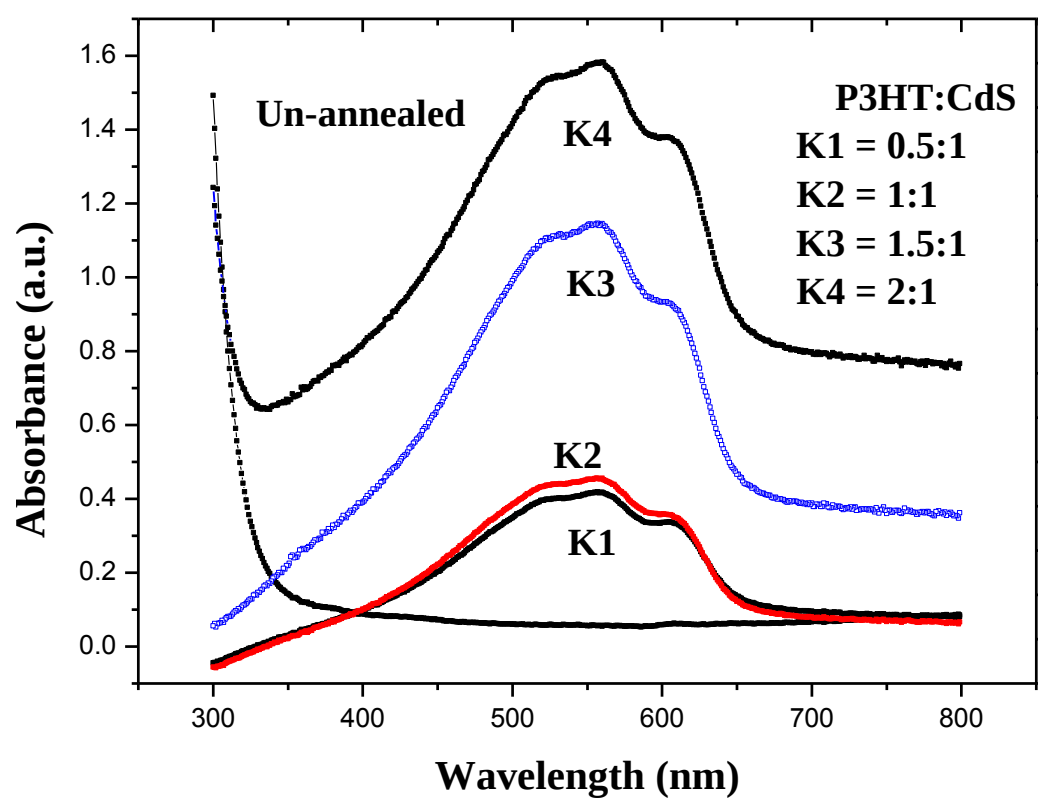


Figure 7-15 (a): UV-visible absorption spectra of P3HT:CdS films before heat treatment.

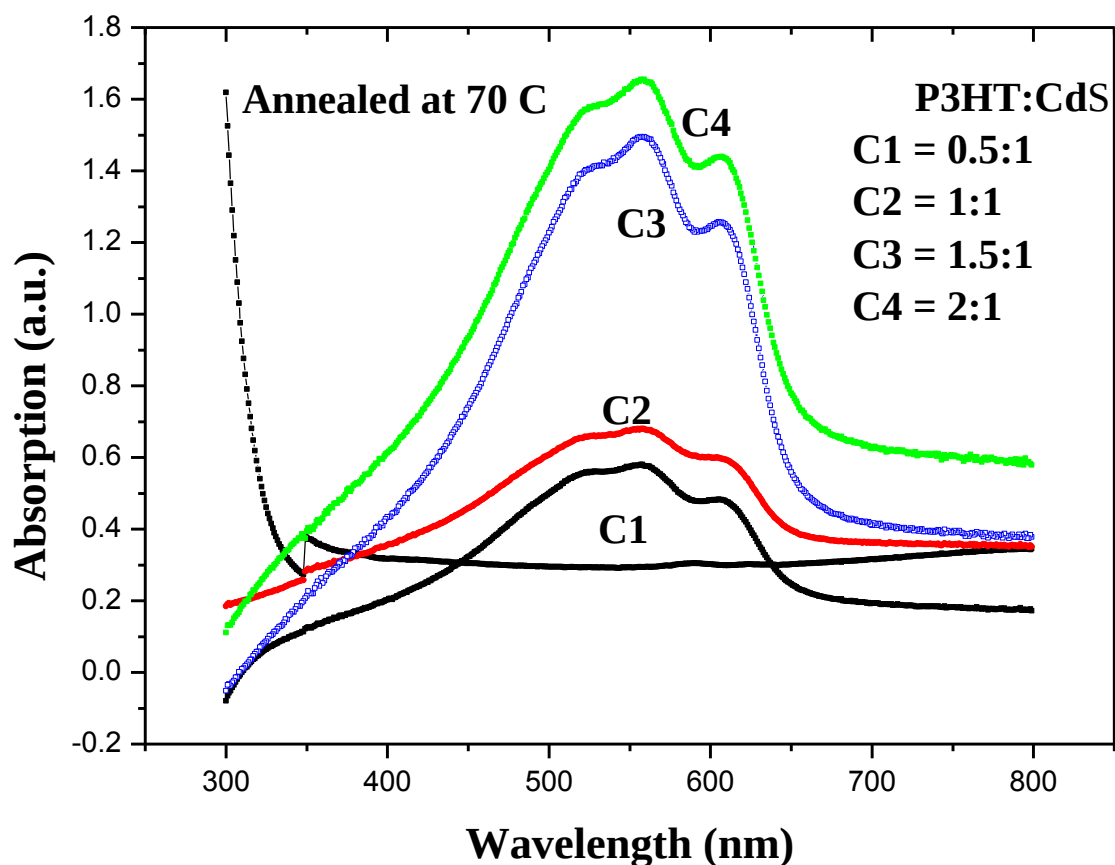


Figure 7-15 (b): UV-visible absorption spectra of P3HT:CdS films after heat treatment.

In order to investigate the efficiency of the charge transfer mechanisms, photoluminescence was performed in the polymer inorganic nanocomposite. Figure 7.16 shows the photoluminescence (PL) spectra of the P3HT:CdS films of (a) an unannealed and (b) an annealed sample at 70 °. The spectra show two prominent peaks for all the samples at ~ 637 and 703 nm. Annealing leads to the broadening and red shifting of the peaks. The peak located at ~ 637 nm (1.95 eV) was assigned to the pure electronic transition (0-0 transition) and the peak at ~ 704 nm (1.76 eV) was assigned to the first vibronic band (0-1 transition) [70], [71]. The red shifts in PL emission after annealing suggest that the polymer chains are π -stacked on top of each other [72]. This is evident in the optical absorption spectrum of Figure 7.15.

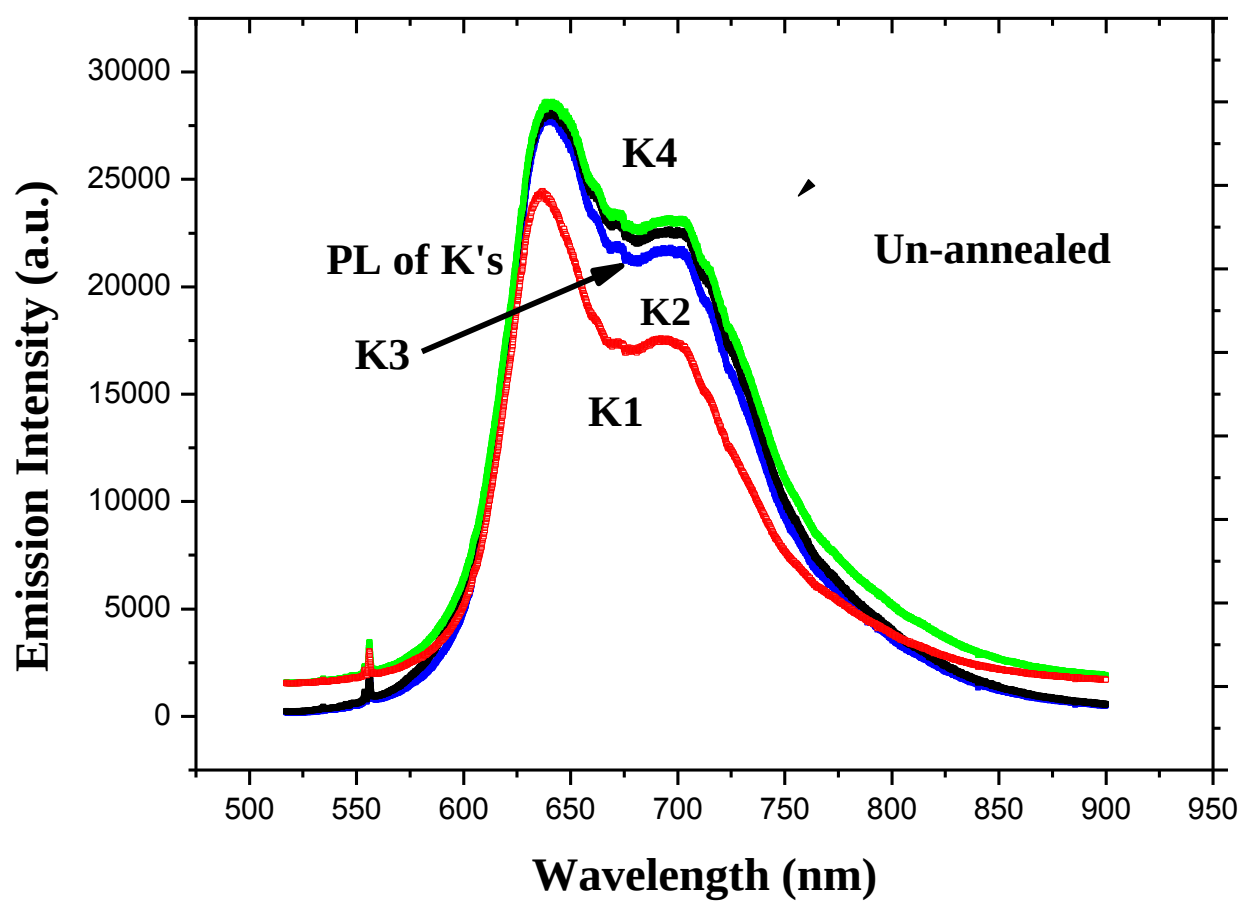


Figure 7-16 (a): PL spectra of P3HT:CdS films before heat treatment.

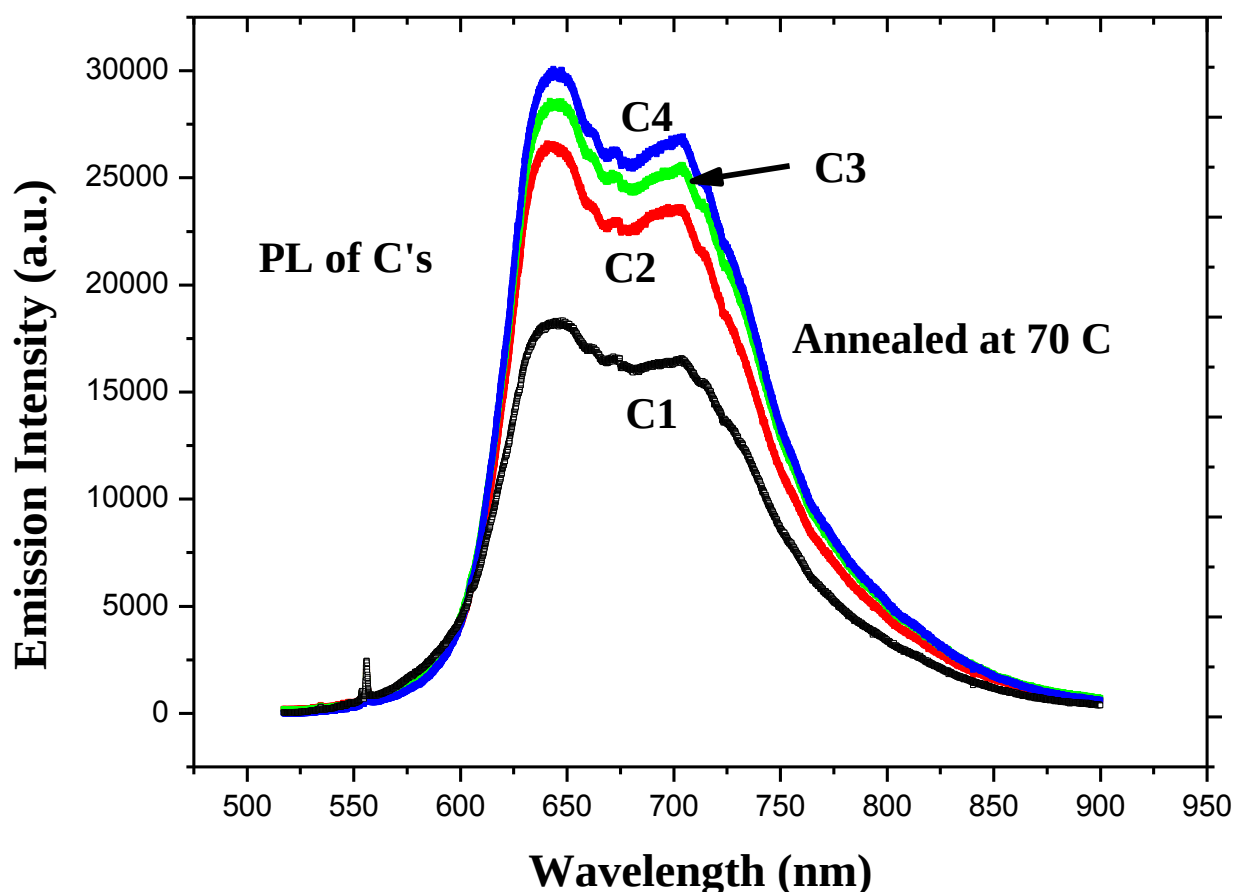


Figure 7-16 (b): PL spectra of P3HT:CdS films after heat treatment.

7.3.4.2 Raman spectroscopy analysis

The Raman spectra of P3HT:CdS films are shown in Figure 7.17 for the (a) unannealed and (b) annealed at 70 °C. From the Raman spectra several peaks were observed. The peaks at ~ 1382 and ~ 1453 cm^{-1} are assigned to C-C stretching vibrations of the thiophene ring and the C=C skeletal stretching respectively [73]. Other bands at ~ 1210 cm^{-1} (inter-ring stretch), ~ 1092 cm^{-1} (C-H bending) and ~ 727 cm^{-1} the (C-S-C bands) were also observed. The Raman intensities of the pre-annealed and annealed samples are about the same, implying that the annealing does not have an impact on the various functional groups.

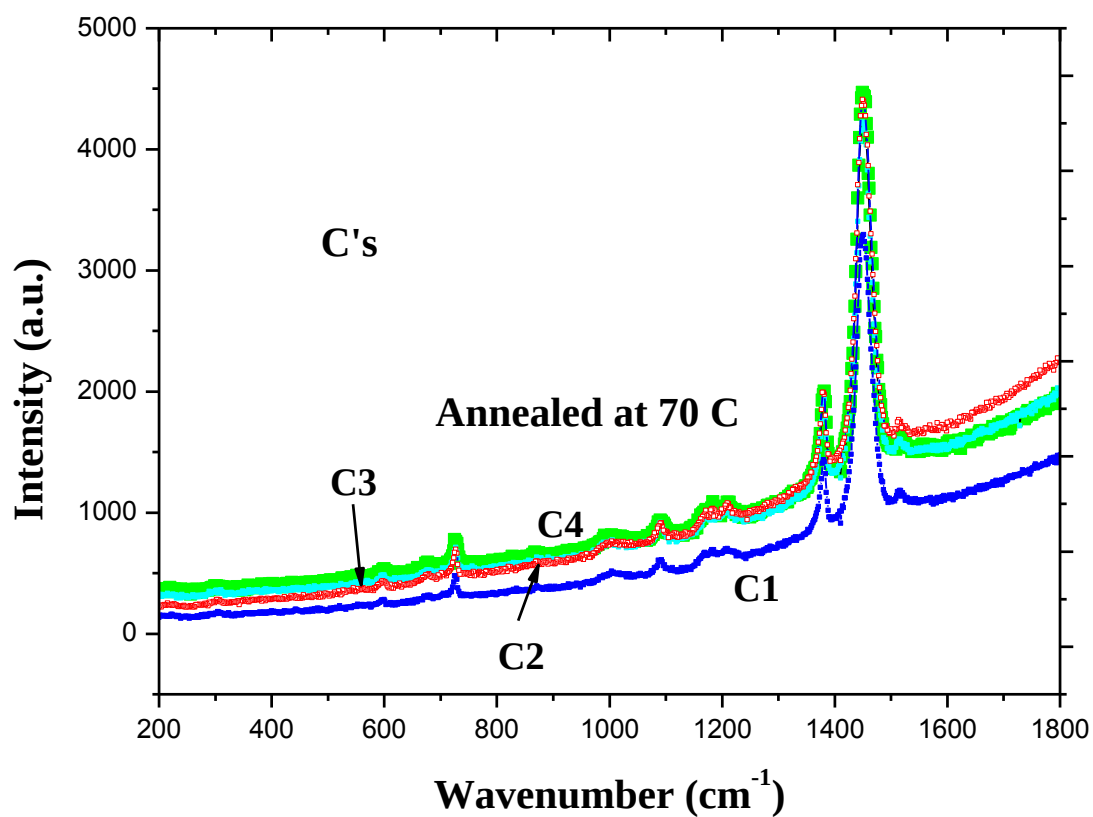
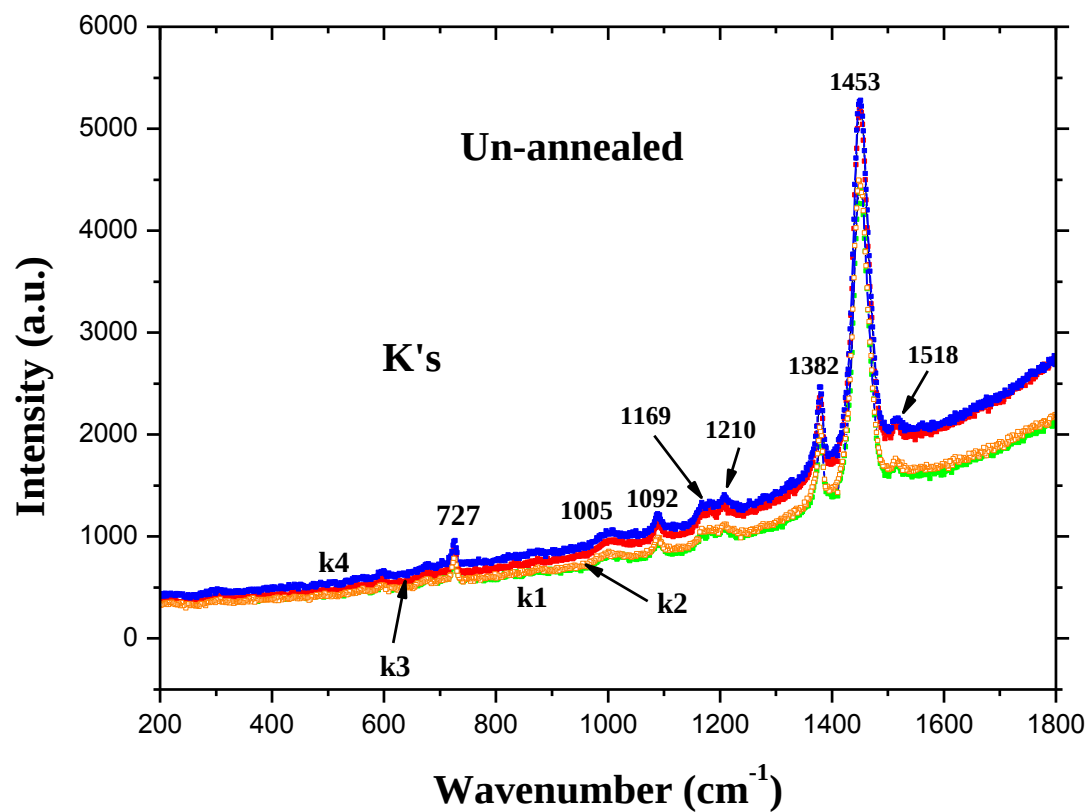


Figure 7-17: Raman spectra of P3HT:CdS films (a) before and (b) after heat treatment.

7.3.4.3 J-V characteristics

To characterize the electrical properties of P3HT:CdS, current density versus voltage (J-V) was measured both in dark conditions and AM 1.5G normal illumination (100mW/cm², 1 sun) at room temperature. Figure 7.18 displays the J-V characteristics of the P3HT:CdS samples on a semi-log scale both in the dark and under light. According to the dark J-V curve, leakage currents in the order of 9.95x10⁻⁵A at -1V are measured and the rectification ratio of 45 is achieved, exhibiting a well-behaving current rectification of p-n junction. The series and shunt resistances extracted from the dark J-V curve are 118 Ω and 7.5 kΩ, respectively.

In the hybrid structure, P3HT acts as the electron donor and CdS as the electron acceptor. It is found that the device performance for the blend fabricated with a P3HT:CdS ratio of (2:1) has better parameters compared to other donor:acceptor ratios. The open circuit voltage (V_{oc}) increases from 0.163 to 0.200 V, the short circuit current (J_{sc}) increased from 1.44 × 10⁻⁵ to 1.61 × 10⁻⁵ mA/cm² and the fill factor (FF) increased from 0.248 to 0.255. The performance of all the devices are summarized in Table 7.2. The device performance enhancement may have come from the improvement of the P3HT:CdS heterojunction interface [74] due to enhance film morphology that promotes charge transfer. In the ideal diode equation, the relationship between dark current and V_{oc} is inferred from [75], [76].

$$J = \frac{R_s}{R_s + R_p} \left\{ J_s \left[\exp \left(\frac{q(V - IR_s)}{nkT} \right) - 1 \right] + \frac{V}{R_p} \right\} - J_{ph}(V) \quad (1)$$

where J is the total current, J_s is the reverse dark saturation current, n is the ideality factor, R_s is the series resistance, R_p is the parallel resistance, V is the bias voltage and J_{ph} is the photocurrent. Setting $J = 0$,

$$V_{oc} = \frac{nkT}{q} \ln \left[\frac{J_{ph}(V_{oc})}{J_s} + 1 - \frac{V_{oc}}{R_p J_s} \right] \quad (2)$$

When $J_{ph}/J_s \gg 1$, V_{oc} is proportional to $\ln (J_{ph}/J_s)$, suggesting that a large J_s results in a reduction in V_{oc} .

The dark current in organic heterojunction solar cells arises mainly from the charge generation and recombination at the heterojunction interface or/and the electron leakage current from the cathode to the anode [61], [77]. The poor result may be attributed to the poor interfacial contact owing to the hydrophilic CdS surface and the hydrophobic P3HT [57]. To determine the nature of the charge transport at various applied the J-V characteristics were plotted in semi-log format.

It appears from the (J-V) behaviour of Figure 7.18 that the dark current is very large and that charge injection mechanisms are limited in the hybrid solar cell. However the behaviour of the V_{oc} in the pristine and under annealed conditions is indicative of morphological changes in the active layer with low inbuilt potential associate with the energy level differences of the LUMO of the P3HT and the valence band of the CdS.

Figure 7.19 shows the semi-log plot behaviour of P3HT:CdS films. The device performance slightly improved with annealing as shown in Figure 7.19 (b).

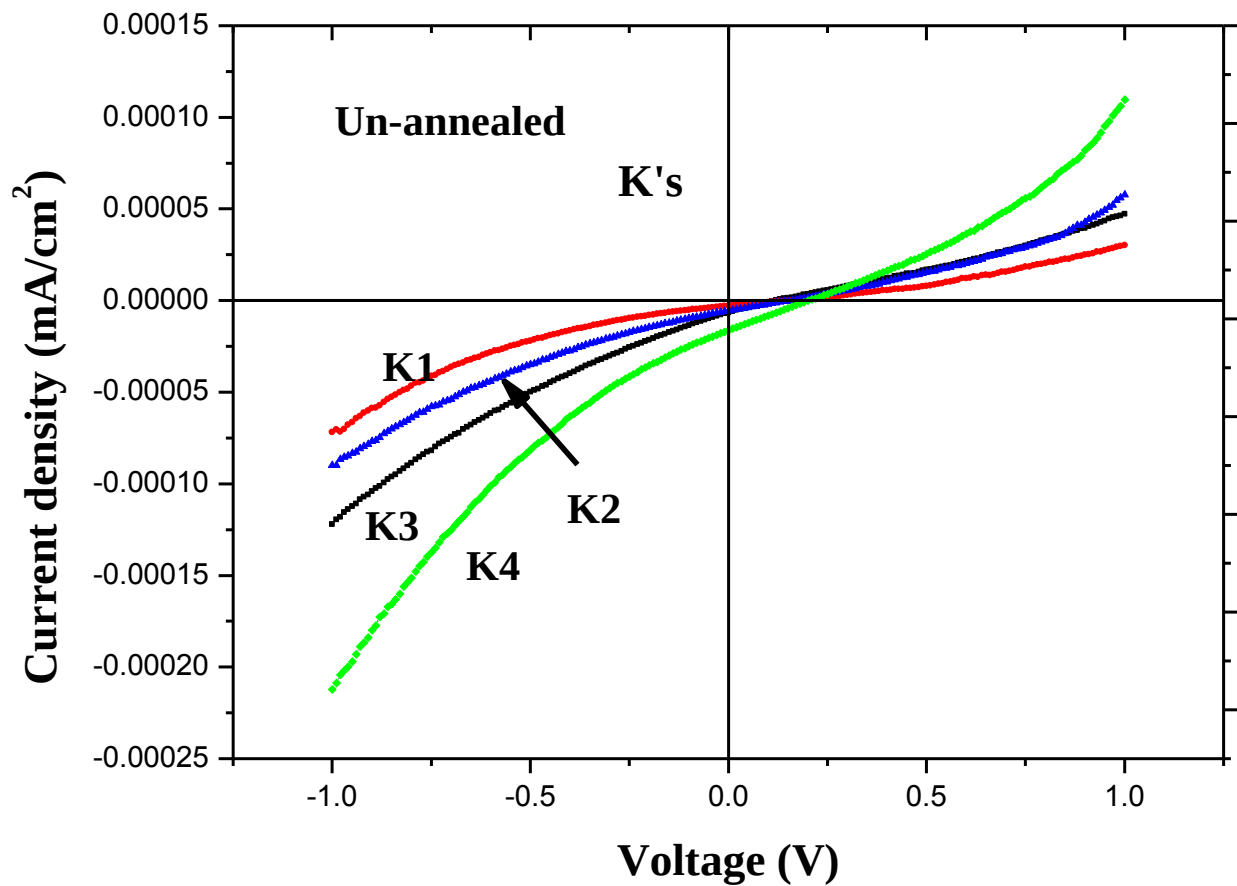


Figure 7-18 (a): J-V characteristics of P3HT:CdS films before heat treatment.

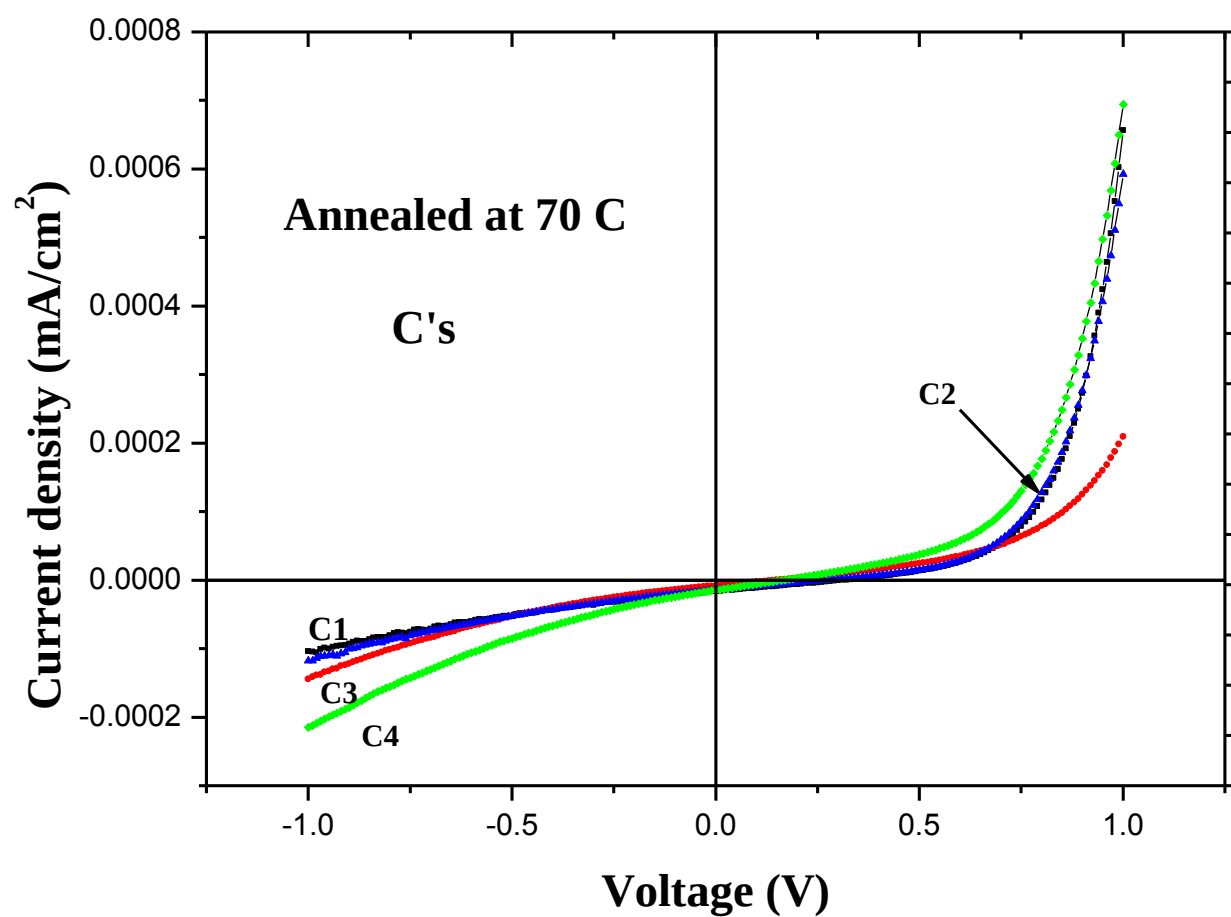


Figure 7-18 (b): J-V characteristics of P3HT:CdS films after heat treatment.

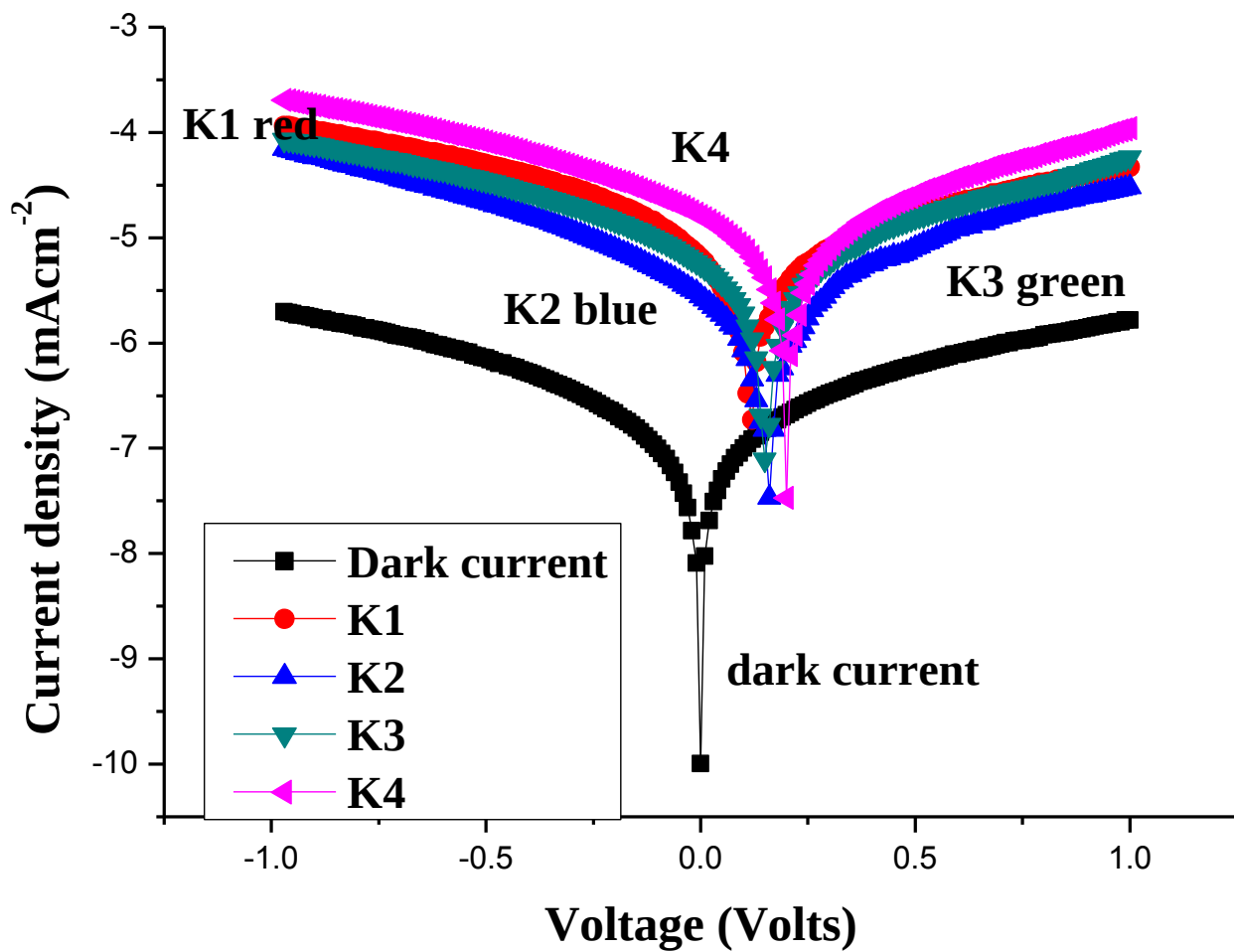


Figure 7-19 (a): Log plot of current density vs. voltage (J-V) behaviour in dark and under AM 1.5G simulated light sunlight illumination of P3HT:CdS films before after heat treatment.

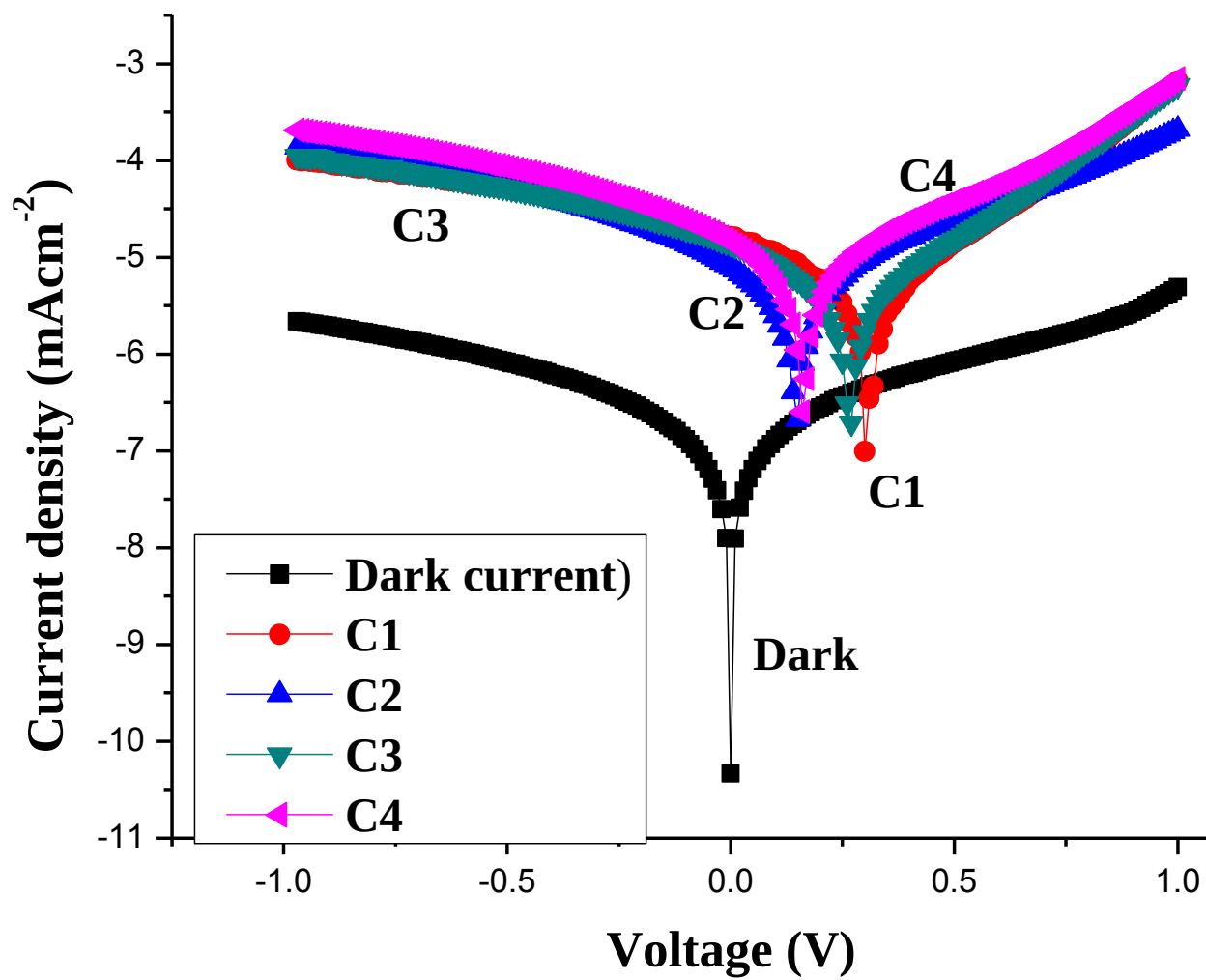


Figure 7-19 (b): Log plot of current density vs. voltage (J-V) behaviour in dark and under AM 1.5 G simulated light sunlight illumination of P3HT:CdS films (a) before and (b) after heat treatment.

Table 7-2: Photovoltaic device parameters of P3HT:CdS films (before and after heat treatment).

Sample	P3HT:CdS ratio	Voc (V)	Jsc (mA/cm ²)	FF	PCE (%)	R _{sh} (kΩ/cm ²)	R _s (kΩ/cm ²)
C1	0.5 : 1	0.3022	1.64×10 ⁻⁵	0.262	0.001	17.1	17.5
C2	1 : 1	0.1456	7.82×10 ⁻⁶	0.255	0.0	19.4	18.6
C3	1.5 : 1	0.2661	1.38×10 ⁻⁵	0.239	0.001	17.3	19.5
C4	2 : 1	0.1631	1.44×10 ⁻⁵	0.248	0.001	10.9	11.4
K1	0.5 : 1	0.1164	6.46×10 ⁻⁶	0.226	0.0	16.3	20.4
K2	1 : 1	0.1618	2.80×10 ⁻⁶	0.241	0.0	43.8	53.0
K3	1.5 : 1	0.1532	5.48×10 ⁻⁶	0.248	0.0	27.0	32.7
K4	2 : 1	0.2004	1.61×10 ⁻⁵	0.255	0.001	11.9	13.5

Cortina-Marrero and co-workers reported that thicker P3HT films have lower Jsc values probably due to the increased of series resistance of the cells [69]. They found that annealing at high temperatures (170 – 190 °C) improved the photovoltaic performance of the P3HT:CdS bilayer solar cells. The FF value was not affected by the polymer thickness.

7.3.5 Conclusions

In summary, hybrid solar cells based on P3HT:CdS blend were fabricated. The samples (P3HT/CdS nanostructures) were prepared with different ratios before and after annealing. We found that the efficiencies of all the fabricated samples are very poor. This may be due to the molecular disorder in the polymer films and possible recombination at the interfaces. The annealing temperature could be the reason for that. Further improvement in the performance could be achieved by increasing the annealing temperature to above 100 °C. There is no increase in the absorption of the CdS samples after the heat treatment at 70 °C this could be because the temperature was low. We could heat the samples at temperature of between 100 and 120 °C to see if there is any effect of the heat treatment.

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Chapter 8: Conclusions and Outlook

8.1 Conclusions

Carbon based nanomaterials have been investigated due to their wide ranging application potential which are driven primarily by their novel size and geometry dependent properties. In this project a facile synthesis method has been used for the fabrication of aligned doped carbon nanotubes with potential for applications as magnetic sensors or hetero-structures. In addition conventional horizontal chemical vapour deposition (CVD) was used to synthesize carbon coated GaN nanostructures with large surface areas for sensor applications. Among the carbon nanostructures that have been studied in this project are multi-walled carbon nanotubes which have been loaded with transition metal based oxides and sulphides for sensor and photovoltaic applications.

8.1.1 Nitrogen doped multi-walled carbon nanotubes loaded with metals (SnO₂ and CdS)

Nitrogen doped multiwall carbon nanotubes (N-CNTs) act as templates for catalyst support due to their large surface area to volume ratio. Besides their high electronic and thermal conductivity make them suitable for sensor applications. Among the metal based compounds that have attracted intensive interest in sensor device are SnO₂ and CdS. However their low thermal stability and low surface area redirected research efforts towards the use of CNT as templates for sensor applications. In this project, nitrogen doped multiwall CNTs have been used as a backbone for SnO₂ and CdS compounds through a CVD based synthesis procedure. The synthesized N-CNT decorated metal based group VI compounds were characterized for structural, morphology and thermal properties using by XRD, TEM, SEM, TGA, Raman and FTIR. SnO₂ nanoparticles were successfully decorated on N-CNT by wet chemical method and their crystalline size was estimated to be ~10 nm from XRD spectra using Scherrer equation. The TEM images revealed that the synthesis achieved a uniform coverage of SnO₂ nanoparticles on the surface of N-CNT. Polycrystalline SnO₂ nanoparticles are observed to be attached to the surface and inside the tubes. Inside the tubes are a mixture of SnO₂ nanoparticles and amorphous carbon. The FTIR spectra of N-CNT_SnO₂ confirm the presence of functional groups (C=C, C=O, O-H).

On the other hand, polycrystalline CdS nanoparticles have been successfully deposited on the surface of N-CNT and their crystallite size was estimated to be ~2nm. The Raman spectrum for N-CNT_CdS shows 3 additional bands located at 293, 589 and 885 cm^{-1} corresponding to the first-order longitudinal-optical (1LO) phonons, the second-order longitudinal-optical (2LO) and third-order longitudinal-optical (3LO) respectively. These three bands belong to CdS nanoparticles. The presence of functional groups (C=C, C=O and O-H) on the surface of N-CNT_CdS have been confirmed by FTIR.

8.1.2 Characterization of aligned nitrogen-doped multi-walled carbon nanotubes

- Conventional CVD was used to synthesize aligned MWCNTs from ferrocene and toluene/acetonitrile mixtures and purified by 55% nitric acid.
- Disorder and defects are introduced into the CNT lattice on N doping.
- Fe-impurities are made up mostly of Fe_2O_3 , Fe_3C , $\alpha\text{-Fe}$ and $\text{Fe-}\gamma$ from the residues embedded within the A-CNTx tubes as determined from Mössbauer spectroscopy.
- Magnetic properties of the A-CNTx were shown to depend on the Fe-residue embedded within the tubes and this was confirmed by SQUID analysis.
- The Fe-residue was predominantly made up of Fe_3C and Fe_2O_3 for the nitrogen doped containing samples ($x = 0.5$ and 1) as determined from Mössbauer spectra.
- The ferromagnetic content of the Fe nanoparticle residue decreased with increased nitrogen content while the paramagnetic doublet (Fe^{3+}) component increased with increased nitrogen content.
- All the samples exhibited magnetic properties (ferromagnetic behaviour). As the nitrogen content increased the M_s values decreased. The magnetization M decreased with increasing nitrogen content. The levels of purification of the samples determined by both EPR and dc susceptibility measurements are in reasonably good agreement, as both methods are very sensitive to magnetic impurities.

8.1.3 Synthesis and characterization of C-GaN nanostructures

GaN nanostructures continue to receive intensive research interest due to their excellent properties. However their application as gas sensors has been limited to elevated temperatures and using costly fabrication procedures such as the MOVPE, MOCVD etc. The use of a horizontal CVD method provides a quick and easy method to fabrication carbon decorated GaN nanostructures for sensor applications at room temperature. To this end, carbon coated GaN (C-GaN) with have been synthesized using two different carbon sources (C_2H_2 and toluene) as well as two different carrier gases (N_2 and Ar). More carbon was coated when the carrier gas Ar as opposed to N_2 was used irrespective of the carbon source. Our observations have revealed the following;

- Acetylene based carbon coated GaN produced a thicker carbon coating (8.3 and 9.4 nm) than their counterparts fabricated with toluene as a carbon source (1.8 nm).
- There is a shift of the A_1 (LO) Raman peak of between 9 and 30 cm^{-1} for the C-GaN samples compared to pure GaN, this could be attributed to phonon confinement.
- The YL bands intensity for all the carbon coated samples were observed to have decreased and the peak positions increases slightly (2.23 – 2.27 eV) compared to pure GaN (2.20 eV).
- The red luminescence (RL) peak present in the pure GaN has its photon energy shifted to downwards side (1.74 eV) after the introduction of carbon.
- The PL peaks are clearly visible in the samples that used toluene as carbon source (C-GaN TN and C-GaN TA) compared to the ones that used acetylene as carbon source.
- The samples that used acetylene as a carbon source have more carbon

The thickness of the carbon layer deposited on the surface of the GaN was estimated to be about 9.4 nm, 8.3 nm and 1.8 nm for C-GaN CN, C-GaN CA and C-GaN TN respectively.

8.1.4 Sensor applications

We have demonstrated for the first time the use of carbon coated GaN as a room temperature sensor. The C-GaN was found to respond to multiple gases (H_2 , CO, NH_3 and CH_4) at low concentration (5 to 100 ppm). The sensitivity of the device is proposed to be due to defects on the surface of the carbon coated GaN. Sensor measurements show that carbon coated device C-GaN

TA has a better sensitivity as compared to C-GaN CN at room temperature. Further development of the sensor could improve on.

- The carbon content obtained in the presence of argon showed a higher % of graphitic-N and a higher C content from XPS data. In addition, the total N content was lower than in the N-doped CSs obtained using hydrogen as a carrier gas

8.2 Recommendations

- The synthesised carbon coated GaN (C-GaN) samples could be possibly use in solar cell applications.
- Hall Effect and temperature dependent measurements needs to be carried out to ascertain the (electron and holes) charge carrier density of the carbon doped GaN structure.
- Gas sensor measurements (C-GaN CA and C-GaN TN) are being carried out at CSIR.
- Low T Raman and PL to show the presence of activated defect levels and their binding energies in C-GaN.
- Further characterisation will be carried out and finally the ultimate goal would be for the material to be use in solar cell fabrication.
- The material N-CNT coated CdS should be test in solar cell applications.
- Metals such as CdS and SnO₂ could be loaded on the synthesised A-N-CNTx and possibly be used in sensor and solar cell applications.
- Optimization of the gas sensing characteristics in N-CNT decorated CuO and the deeper understanding of the mechanisms involved in the response and sensitivity of the sensor to select gases.

APPENDIX

Table S1: % concentration of types of N and C configurations in the A-CNTx

Samples	C-C (eV)	C=O (eV)	O- C=O (eV)	O-C (eV)	π - π^* (eV)	Pyridinic (eV)	Pyrrolic (eV)	Graphitic (eV)	NOx (eV)	Chemis orbed (eV)
X=0	64.74	13.78	8.07	10.29	3.11	-	-	-	-	
X=0.5	67.12	13.03	9.35	6.42	4.08	19.78	16.04	24.06	32.57	7.55
X=1	64.41	18.56	7.24	7.22	2.57	21.43	11.79	39.45	21.29	6.05