

Republic of Iraq Ministry of Higher Education and Scientific Research University of Diyala College of Science Department of Physics



# Synthesis and Physical Studies with Applications of Carbon Nanotubes by CVD Technique

A thesis Submitted to the Council of the College of Science University of Diyala in Partial Fulfillment of Requirements for the Degree of Doctor of Philosophy in Physics By

# **Intessar Kadhum Abd**

**Supervised By** 

Prof. Dr. Ziad T. Khodair Assist Prof. Dr. Firas H. Abdulrazzak

2020 A.D.

1442 A.H.

إِنَّا فَتَحْنَا لَكَ فَتُحًا مُّبِيْنَا لِّيَغُفِرَ لَكَ اللَّهُ مَا تَقَدَّمَ مِنْ ذَنْ وَمَا تَأَخَّرَ وَيُتِمَّ نِعْبَتَهُ يكك صراطا لمستق وَّيَنُصُرَكَ اللهُ نَصُرًا عَزِيُزًا

### Acknowledgement

First of all I thank the Almighty *Allah*, whose Grace enabled me to continue this work and overcome all difficulties and our prophet *Muhammad* (peace and blessings of Allah be upon him) who invites us to science and knowledge.

I would like to express my sincere appreciation and deep gratitude to my supervisors, **Prof. Ziad T. Khodair & Assist Prof. Firas H. Abdulrazzak** for suggesting the topic of this thesis, guidance, suggestions and continuous encouragement throughout the research work. I would like to express my profound gratitude to **Prof. Dr. Nabeel A. Bakr , Prof. Dr. Sabah A. Salman and Assist Prof. Dr.Buthina** for them kind cooperation and constant support and I am highly indebted for them constant encouragement throughout my Ph.D. study in the Department of Physics, College of Science, University of Diyala.

Special thanks are extended to the University of Diyala, College of Science, specially The dean of College of Science, **Prof. Dr. Tahseen H. Mubarak** and all the Staff of the Department of Physics for their assistance.

I would also like to thank the staff of the Library of College of Science( Adnan, Raafat and Anwar), who continued to provide excellent service, tireless support and scientific resources to all students.

I do not forget to thank staff for the Department of Chemical ,College of Education for Pure Science, University of Diyala for their assistance.

My greatest gratitude for **My husband (Dr. Ammar Abdulsattar Mohammad)** for his endless support.

My greatest indebtedness goes to my **Father, Mother and Brothers** for their valuable advice, and to all my **friends** for their endless support.

 Nasser, I., Tareq, Z., & Habeb, F. (2019, July). Effect of Molecular Interaction Towards Homogenous Diameters for Synthesized MWCNTs from Methanol / Butanol mixture by CVDs. In IOP Conference Series: Materials Science and Engineering (Vol. 571, No. 1, p. 012063). IOP Publishing

**2.** Intessar K. Abd, Firas H. Abdulrazzak, Ziad T. Khodair, "Synthesis of MWCNTs from Methanol/Butanol Mixture by Catalytic Chemical Vapor Deposition and Application to Synthesized Dye Sensitizer Solar Cell".In AIP Conference Series: Materials Science and Engineering (Vol. 2213, No.1, pp.020318). AIP Publishing



In this study, for the first time in the laboratories of the Department of Physics - College of Science - University of Diyala, the manufacture of multiwalled carbon nanotubes (MWCNT) was made using the chemical vapor deposition system (CVD), which was prepared and manufactured most of its parts manually. As different ratios were mixed Of methanol and butanol as a primary source of carbon and the use of both viruses as a catalyst and hydrogen peroxide for purification.

used were techniques Raman spectroscopy, Field Emission Scanning Electron Microscopes (FE-SEM), Transmission electron microscopy (TEM) (TEM), energy dispersion spectroscopy (EDS), and x-ray diffraction (x-ray).

The Raman spectrum showed that the composition contains two main beams and for all samples: the G-band within the range of (1570-1585) cm<sup>-1</sup>, and the D-beam at the range (1300- 1340-) cm<sup>-1</sup> which indicates the pattern of elongation (sp<sup>2</sup>), and (sp<sup>3</sup>) respectively.

Pictures of FE-SEM showed the formation of carbon tubes in various and various forms and for all samples, with a clear directional growth of the samples that were made from mixing alcohol ratios: (Methanol 75% + Butanol 25%, Methanol 50% + Butanol 50%), and the rate was obtained diameters are within (20-200) nm and lengths are within (1000-4200)  $\mu$ m.

As for images TEM, they demonstrated the formation of multi-walled carbon nanotubes with high clarity. EDS analyzes also showed the emergence of carbon, which is the main material for forming tubes and the appearance of both oxygen and iron. The results of x-ray diffraction analyzes showed that all samples are polycrystalline and hexagonal type with a predominant direction (002).

After conducting the diagnostic process, the sample produced from (Methanol 50% + Butanol 50%) was used in the following applications due to growth in the straight direction of the carbon tubes as well as obtaining a good sample of (0.9 g) after the purification process as follows: -

- **First :** the manufacture of an sensor for ethanol gas, and if the results show an increase in sensitivity when increasing the flow rate of the gas.
- **Second :** the manufacture of a DSSC dye solar cell. The multi-walled nanotubes of both commercial and produced types were first loaded in 0.005, 0.01 ratios on titanium dioxide. This is precipitated as a paste on the base of the FTO glass by the method of the doctor blade, and then plasticized at 450° C for 30 minutes. The optical properties of these films were studied before and after the annealing process.

The highest efficiency of the DSSC4, which was 0.83%, was obtained.

### **List of Contents**

No.	Subjects	Page
		No.
	Chapter One	
	Introduction and Basic Concept	
1.1	Introduction	1-2
1.2	Carbon atom	3-5
1.3	Strategy of synthesized Carbon Nanotubes	6
1.3.1	Arc-discharge method	6-7
1.3.2	Laser ablation method	7-8
1.3.3	Chemical vapor deposition CVD	8-10
1.3.4	Mechanism of Growth CNT' into CVD	10-12
1.4	Literature Review of CNT	13-18
1.5	Aim of the Research	18
	Chapter two	
	Theoretical Background	
2.1	Carbon nanotubes	19-20
2.2	Structure of Carbon Nanotubes	20-21
2.3	Types of Carbon Nanotubes	21-23
2.3.1	Types on the basis of chirality	23-25
2.3.2	Classification by Conductivity	25
2.4	Defects of CNTs	25-27
2.5	Carbon Nanotubes Properties	28
2.5.1	Electrical Conductivity	28
2.5.2	Strength And Elasticity	28
2.5.3	Thermal Conductivity And Expansion	29
2.6	Overview of CNT Characterization Methods	29
2.7	Raman Spectroscopy	30
2.7.1	Basic Principles and Instrumentation	31-33
2.7.2	Radial Breathing Mode (RBM)	33-34
2.7.3	The G-band	34
2.7.4	The D-band	34-35
2.8	XRD Application in CNT Characterization	35
2.8.1	XRD Fundamental Principle	35-37
2.8.2	XRD Experiments for CNTs	37-39
2.9	Structural Parameters:	39
2.9.1	Lattice constants $(a, c)$ of tetragonal structure	39
2.9.2	Average crystallite size (D <sub>av</sub> )	40
	a. Scherer's method ,b. Williamson-Hall method (H.W)	

2.9.3	Dislocation density and number of grains	41
2.10	Scanning Electronic Microscopy SEM	41-43
2.11	Transmission Electron Microscopy TEM	44-46
2.12	Optical Properties of Crystalline Semiconductors	47
2.12.1	Absorbance (A)	47
2.12.2	Absorption coefficient ( $\alpha$ )	47-48
2.12.3	Optical Energy Gap (g)	48
2.13	Some Optical Parameters	48
2.13.1	Extinction Coefficient (K <sub>o</sub> )	48-49
2.13.2	Dielectric Constant (ɛ)	49
2.14.	Nanotubes Applications	49
2.14.1	Energy Storage	49-50
2.14.2	Gas Sensors	50-51
2.14.3	Dye Sensitized Solar Cells (DSSCs)	51-53
	Chapter three	
	Experimental Work	
3.1	Introduction	54
3.2	CNTs Synthesis Process	54
3.2.1	Chemical Vapor Deposition Unite	54-56
3.3	Chemicals and Materials	57
3.4	Preparation of substrates	58
3.4.1	Substrate cleaning	58
3.4.2	Catalyst Preparation	58-59
3.5	Carbon precursor	59-60
3.5.1	Carrier Gas Flow	61
3.5.2	Time of Growth	61
3.5.3	Growth Temperature	61
3.5.4	Setting of the Tube Furnace	62
3.6	Experimental details in CVD	63
3.6.1	Purification Process	64
3.7	Preparation of MWCNT's thin film	64
3.7.1	Experimental setup of gas sensor	64-65
3.8	synthesized of DSSC	66
3.8.1	Preparation of Glass Substrates	67
3.8.2	Preparation of MWCNTs /TiO <sub>2</sub> Nano composite	67-68
3.8.3	Preparation of Working Electrodes (Photo	69-70
	anode)	
3.8.4	Preparation of electrolyte and counter electrode	70-71
3.8.5	Electrolyte of DSSCs	71

3.8.6	Solar cell assembly and measurements	72-73
3.9	Characterizations techniques	73
3.9.1	X-Ray Characterization	74
3.9.2	SEM Characterizations	74
3.9.3	TEM characterization	75
3.9.4	Raman spectroscopy characterization	75
3.9.5	Optical Measurements	75
	Chapter Four	
	Result and discussion	
4.1	Introduction	76
4.2	Raman spectroscopy	76-81
4.3	Morphological Analysis	81
4.3.1	FE-SEM analysis for synthesized MWCNT's	81-86
4.3.2	TEM analysis for synthesized MWCNT's	87
4.3.3	Energy dispersive X-ray spectroscopy (EDS)	88-91
4.4	Structural Properties of CNT	91
4.4.1	XRD Analysis of MWCNT's	91-94
4.4.2	The crystallite size $(D_{av})$	95
	I. Calculation of crystallite size using Scherer's	
	formula:	
	analysis	
4.4.3	Dislocation Density ( $\delta$ )	96-97
4.5	Gas Sensing Result	98
4.5.1	Sensing Characteristics at Room Temperature	98-99
4.5.2	Gas Sensing Characterization	99-103
4.6	Dye Sensitized Solar Cell Result	104
4.6.1	FE-SEM morphological structure	104-107
4.6.2	Energy dispersive X-ray spectroscopy (EDS)	108-109
4.6.3	Optical Properties	110-115
4.6.2	Optical Energy gap $(E_g)$	115-121
4.6.3	Extinction Coefficient $(K_0)$	122-123
4.6.4	Dielectric Constant (ɛ)	123-126
4.7	Current-Voltage characterization	126-131
4.8	Conclusions	131-132
4.9	Future work	132
	References	133-154

### **List of Tables**

No.	Title	Page No.
3-1	Chemical and Materials	57
4-1	Represented style and contented the samples	78
4-2	Raman value of peaks D, G and intensity $I_D/I_G$ for	78
	MWCNT's	
4-3	The lengths and diameters of synthesized MWCNT's	86
	and weight of samples after preparation	
4-4	The quantitative EDS results for all samples	88
4-5	The value of $(2\theta)$ for peaks of synthesized MWCNT's	94
4-6	Structural parameters for all samples and comparison	96
	between Scherrer and W.H methods of MWCNT's.	
4-7	Response time ,recovery time and Sensitivity% of	102
	MWCNT film.	
4-8	Represented TiO <sub>2</sub> with different MWCNT's	105
	concentration and type	
4-9	$TiO_2$ and $TiO_2$ with different ratios of the MWCNT's	112
	films.	
4-10	The energy gap for $TiO_2$ /MWCNT films.	119
4-11	The energy gap for TiO <sub>2</sub> /MWCNT films.	119
4-12	TiO <sub>2</sub> ,TiO <sub>2</sub> /MWCNT nanostructures produced anode	128
	were used to assemble five DSSC's	
4-13	The photovoltaic parameters of DSSC's.	128

# **List of Figures**

No.	Title	Page
1 1	Carbon allotronas in four different erustellographie	110.
1-1	structures	4
1_2	a a fullerene b a carbon nanotube c granhene	4
1-2	a. Electronic configuration of a carbon atom	5
1-5	b Representation of its atomic orbitals	5
1-4	Basic a helxagonal and orbital structure of graphene	5
1-5	Schematic diagram showing the arc discharge method	7
1-6	Schematic of laser ablation	8
1-7	Schematic of thermal CVD	9
1-8	Schematic representation of the two typical CNT growth	12
	modes,(a) tip growth mode and (b) base growth mode CNT	
2-1	Structure of Carbon Nanotubes , (a) SWCNT ,	21
	(b) MWCNT	
2-2	Types of carbon nanotubes	23
2-3	a. Geometries of CNT, b. arm-Chair, c. Zig Zig, d. chair	24
2-4	(color online) Doping defects	26
2-5	The S-W formation in the hexagonal lattice of CNTs:	27
	(a) pristine lattice and (b) SW-defected lattice	
2-6	Atomic vacancies present on outer walled of DWCNT	27
2-7	The photograph of Raman spectroscopy.	30
2-8	The diagram showing the type of transition of the electrons	32
	and the Rayleigh and Raman scattering[	
2-9	Raman Spectrum of SWCNT, DWCNT and MWCNT	33
	samples	
2-10	Schematic to derivate the Bragg's Law .X-ray (arrows) are	37
	reflected by crystallographic planes separated by a distance d	
2-11	Schematic diagram of basic principle of XRD for CNT	39
2-12	Schematic of a Scanning Electron Microscopy	43
2-13	Schematic of core components of a TEM microscope	46
2-14	Structure of dye –sensitized solar cells (DSSCs)	53
3-1	Schematic diagram for plane of synthesis MWCNT's in this	56
	work.	
3-2	The quartz sample: (a) before deposition catalyst	59
	b) after deposition catalyst.	
3-3	MWCNT's as carbon soot formation on quartz sample	60

3-4	(a) the furnace which is used in this work	62
	(b) schematic of the growth temperature.	
3-5	schematic diagram of CVD system	63
3-6	photos for the process of purification the synthesized	65
	MWCNT's (a) MWCNT deposition on quartz surface, (b)	
	sample after clean by ethanol,(c)solution of MWCNT, (d)	
	MWCNT as powder after drying, (e)MWCNT with $H_2O_2$ ,(f)	
	MWCNT purification as powder after drying.	
3-7	Preparing scheme of the DSSC	66
3-8	Show , (a) solution of $0.5g$ TiO <sub>2</sub> ,(b) solution of $0.2 g$	70
	MWCNT +20ml H <sub>2</sub> O <sub>2</sub>	
3-9	shows the different rate of solution for TiO <sub>2</sub> /MWCNT,	70
	(a)0.01 MWCNT,(b) 0.005MWCNT	
3-10	photos for the process of prepare an anode ,(a)	72
	TiO <sub>2</sub> /MWCNT films before annealing, (b) films annealing ,(c)	
	solution of dye, (d) films in solution of dye, (e) films after	
	immersing in a solution of dye	
3-11	Photos for preparation of cathode, (a) the film from silver	73
	nitrate, (b) the films after coated by black soot.	
3-12	photos for Solar Cell assembly	74
3-13	photo for Cell Tester MODEL (CT100 AAA).	75
4-1	Raman shift for the synthesized MWCNT's from	79
	Methanol 100%.	
4-2	Raman shift for the synthesized MWCNT's from	79
	Methanol 75% + Butanol 25%	
4-3	Raman shift for the synthesized MWCNT's from Methanol	80
	50% + Butanol 50% .	
4-4	Raman shift for the synthesized MWCNT's from	80
	Methanol 25% + Butanol 75% .	
4-5	Raman shift for the synthesized MWCNT's from	81
	Butanol 100% .	
4-6	FE-SEM images of Sample1 (a) 15 000x (b) 30 000x (c) 60	82
	000x (d) 120 000x magnifications	
4-7	FE-SEM images of Sample2 (a) 15 000x (b) 30 000x (c) 60	83
1.0	000x (d) 120 000x magnifications	
4-8	FE-SEM images of Sample3 (a) 15 000x (b) 30 000x (c) 60	84
1.0	000x (d) 120 000x magnifications	0-
4-9	FE-SEM images of Sample4 (a) 15 000x (b) 30 000x (c) 60	85
4.10	000x (d) 120 000x magnifications	07

	000x (d) 120 000x magnifications	
4-11	TEM photographs of synthesized MWCNT's using CVD	87
4-12	EDS analysis of sample1 by CVD at 700°C	89
4-13	EDS analysis of sample2 by CVD at 700°C	89
4-14	EDS analysis of sample3 by CVD at 700°C	90
4-15	EDS analysis of sample4 by CVD at 700°C	90
4-16	EDS analysis of sample5 by CVD at 700°C	91
4-17	X-ray diffraction pattern of synthesized MWCNT's.	93
4-18	The W.H analysis of synthesized MWCNT's.	97
4-19	FE-SEM image of MWCNT's film at (a) 150 000x (b) 30	99
	000x (c) 50 000x (d) 120 000x magnifications	
4-20	The varation of resistance with time for MWCNT film	100
	synthesized at 700°C, ethanol gas sensing , (a) 250ppm,(b)	
	500ppm,(c)750 ppm.	
4-21	The variation of sensitivity with time for MWCNT film,	101
	ethanol gas sensing, (a) 250ppm,(b) 500ppm,(c) 750ppm.	
4-22	Plot of Sensitivity vs. gas ratio for MWCNT film.	102
4-23	Plot of response time and Recover time vs. gas ratio	103
	of MWCNT sensor.	
4-24	Show the FE-SEM surface morphological structure of image1	105
4-25	Show the FE-SEM surface morphological structure of image2	106
4-26	Show the FE-SEM surface morphological structure of image3	106
4-27	Show the FE-SEM surface morphological structure of image4	107
4-28	Show the FE-SEM surface morphological structure of image5	107
4-29	EDS analysis of image1 using CVD	108
4-30	EDS analysis of image2 using CVD	108
4-31	EDS analysis of sample3 using APCVD	109
4-32	EDS analysis of image4 using CVD	109
4-33	EDS analysis of image5 using CVD	109
4-34	The absorption spectrum of Ruthenium Z907dye	110
4-35	Absorbance vs. wavelength of $TiO_2$ /MWCNT films,	112
	before annealing.	
4-36	Absorbance vs. wavelength of $TiO_2$ /MWCNT films,	113
	after annealing.	
4-37	The Relation between absorption coefficient and photon	114
	energy of TiO <sub>2</sub> /MWCNT films before annealing	
4-38	The Relation between absorption coefficient and photon	115
	energy of TiO <sub>2</sub> /MWCNT films after annealing	
4-39	The energy gap for TiO <sub>2</sub> /MWCNT films before	117

	annealing temperature.	
4-40	The energy gap for TiO <sub>2</sub> /MWCNT films after	118
	annealing temperature.	
4-41	The energy gap for TiO <sub>2</sub> /MWCNT films before	120
	annealing temperature	
4-42	The energy gap for TiO <sub>2</sub> /MWCNT films after	121
	annealing temperature.	
4-43	The relation between the extinction coefficient and	122
	wavelength for TiO <sub>2</sub> /MWCNT films at different	
	concentrations before annealing.	
4-44	The relation between the extinction coefficient and	123
	wavelength for TiO <sub>2</sub> /MWCNT films at different	
	concentrations after annealing.	
4-45	The relation between the real part of dielectric constant ( $\varepsilon_1$ )	124
	and photon energy for TiO <sub>2</sub> /MWCNT films at different	
	concentrations before annealing.	
4-46	The relation between the real part of dielectric constant ( $\varepsilon_1$ )	125
	and photon energy for TiO <sub>2</sub> /MWCNT films at different	
	concentrations after annealing.	
4-47	The relation between the imaginary part of dielectric constant	125
	( $\varepsilon_2$ ) and photon energy for TiO <sub>2</sub> /MWCNT films at different	
	concentrations before annealing.	
4-48	The relation between the imaginary part of dielectric constant	126
	$(\varepsilon_2)$ and photon energy for TiO <sub>2</sub> /MWCNT films at different	
	concentrations after annealing.	
4-49	Light I-V Measurement ( Test report ) for DSSC1	129
4-50	Light I-V Measurement ( Test report ) for DSSC2	129
4-51	Light I-V Measurement ( Test report ) for DSSC3	130
4-52	Light I-V Measurement ( Test report ) for DSSC4	130
4-53	Light I-V Measurement (Test report) for DSSC5	131

# List of Symbols

Symbol	Meaning
Å	Angstroms
CNTs	Carbon nanotubes
HRTEM	High-Resolution Transmission Electron Microscope
MWCNT	Multi-Wall Carbon Nanotube
SWNTs	Single-Walled Carbon Nanotubes
nm	nanometer
CVD	Chemical Vapor Deposition
EDS	Energy dispersive
FE-SEM	filed emission scanning electron microscopy
0-D	Zero- dimension
1-D	One- dimension
2-D	Two- dimension
d	diameter
PVD	physical vapor deposition
ACNTs	Aligned Carbon Nanotubes
FC-CVD	Floating Catalyst Chemical Vapor Deposition
VACNTs	Vertically Aligned Carbon Nanotubes
APCVD	Atmospheric Pressure Chemical Vapor Deposition
BBCNT	Bamboo carbon nanotubes
CSCNT	Cup-stacked carbon nanotubes
RBM	Radial Breathing Mode
Dav	Average crystallite size
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
TCVD	Thermal chemical vapor deposition
FWCNT	Few Wall Carbon Nanotube
XRD	X-ray diffraction
CNO	carbon Nano-onion
CDC	carbide derived carbon
CNF	carbon nanofibers
DWCNT	Double-walled carbon nanotubes
eV	Electron Volt
$R_{gas}$	Sensor Resistance
Sccm	Standard centimeter cubic per minute



#### **1.1. Introduction**

Nano-materials exhibit interesting physical properties distinct from both the molecular and broad scales, presenting new opportunities for physico-chemical as well as biomedical researches and applications in various areas of chemistry, biology and medicine. The unique chemical, physical and mechanical properties of carbon nanotubes have stimulated extensive investigation since their discovery in early 1990s by Iijima. Although there have been tremendous advances in the fabrication of Carbon Nanotube , the integration of these nanostructures into successful applications and large-scale production processes are yet not very smooth [1].

Nanotechnology and Nano-science are about controlling and understanding matters on sub-micrometer and atomic scale. By definition they are exciting multidisciplinary fields which involve the design and engineering of objects or tools, characterization, production, and application of structures, devices, and systems by controlled manipulation of size and shape at nanometer scale. Nano-materials have sizes ranging from about 1nm up to several hundred nanometers, comparably to many biological macromolecules such as enzymes, antibodies, and DNA plasmids [2].

CNTs have unique nanostructures with remarkably mechanical, thermal and electrical properties, which made them highly attractive for the use as reinforcement in nanotube based composite materials [3]. Mostly these exceptional characteristics are predicted for a CNT which is ideal and far from CNTs currently being produced. CNTs are mostly taken more than micrometer in length and few nanometer less than 100 nm in diameters.

Several studies had concern with CNTs in many fields such as synthesized process, properties, and applications, all trying to reach the best conditions of the process of manufacturing, purification and diagnostics to obtain a perfect application.

CNTs have a large and varied chemical, optical, thermal, electronic and mechanical behaviors. Many manufacturing techniques such, the methods of chemical vapor deposition CVD, Arc discharge and laser ablation, but the CVD technique had been agreed to remain the best and better way to manufacture carbon nanotubes for many reasons. The important of CVDs can be related to inexpensive, uncomplicated, more adaptable and flexible to control manufacturing conditions[4].

Carbon has several allotropes including amorphous, graphite and diamond. Cyclacenes, nanotubes and fullerenes are accepted as the fourth form of solid carbon. The discovery of carbon nanotubes (CNTs) has sparked powerful research in the past decade. The CNTs unique chemical and physical properties suggest their promising applications in the creation of new nanomaterial. Many research groups have tried to synthesize new nanotubes using elements other than carbon, Kroto and Iijim [5-7] are considered to be establish carbon nanotubes science, either because of the precedence in find the initial imaging that made these names. Iijima the most prominent among them due to "his remarkable findings caused the scientific community focus on nanotube research".

In this study, the CVDs system was used to synthesize CNTs by mixing different ratios of alcohol (methanol and butanol) at 700 °C, with using Fe as a catalyst for precipitation. The products were characterized through filed emission scanning electron microscopy (FE-SEM), Raman spectroscopy, X-ray diffraction with transmission electron microscopy (TEM) and Energy dispersive (EDS).

#### 1.2. Carbon atom

Carbon if the sixth element in the periodic table element, Carbon has six electrons that allows bonding with different atoms and hybridization. Many nanomaterials can be formed by carbon atoms only such as Graphene, planer, tubular and spherical graphite [8].

Another litterateurs reported that carbon nanomaterials can be include fullerenes, CNT, and monocrystalline graphite: graphene as shown in Figure (1-1) which is within (0-D, 1-D,2-D) respectively are the common and famous examples of  $sp^2$  hybridization [9]. The new generation of carbon family behave the same hybridization but showed variant in physical and chemical properties as presented in Figure (1-2) [4, 10].

Moreover, the isolated atoms of carbon having four valance electrons in outer orbits 2p and 2s is shown in Figure (1-3) [11]. The graphene structure comprises unite hexagonal carbon atoms as presented in Figure (1-4a) and Figure (1-4b) which reported the four orbitals mixture forming with each ether new orientations paving for the new physiochemical properties [12].

The three  $\sigma$  bonds amongst carbon atoms are formed because of the hybridization of sp<sup>2</sup> while being positioned inside the plane, whereas the  $\pi$  bonds which are out the graphene sheet's plane are responsible for many physical properties. Hybridization sp<sup>2</sup> performs are crucial role in alternating chemical and physical carbon materials' properties in classic and advance classifications, because of the process of re-hybridization, surface curvature and containment of  $\pi$  and  $\sigma$  bonds [12, 13].



Fig.(1-1): Carbon allotropes in four different crystallographic structures [9].



Fig.(1-2): a. a fullerene, b. a carbon nanotube, c. graphene [10].



Fig.(1-3): a. Electronic configuration of a carbon atom , b. Representation of its atomic orbitals [11].



Fig.(1-4): Basic a hexagonal and orbital structure of graphene [12].

#### 1.3. Strategy of synthesized Carbon Nanotubes

The methods of synthesis generally include, Laser Ablation, Arcdischarge and deposition of chemical vapors are utmost significant techniques utilized for the carbon nanotubes production. This section describes the elaborative carbon nanotubes' significance. Carbon nanotubes are not impurities of their size and type depending on the type of technique used to produce it. The techniques listed below produce carbon nanotubes in the form of powders containing small parts of the impurities, and other carbonaceous particles as well for example, amorphous carbon, nanocrystalline graphite, fullerenes & various metals normally, Ni, Co, Fe and Mo were presented in form of crystals throughout the synthesis process.

#### 1.3.1. Arc-discharge method

To obtain CNTs with a few structural defects using the arc discharge method are produced by arc discharge using very high temperatures (above 1700°C). This method contains a reactor with high voltage two graphite electrodes, a water cooled trap and a vacuum chamber of stainless steel. Moreover, the initial step is Arc discharge for recognition and production of CNTs Figure (1-5).

The principle of action is to evaporate carbon rod was separated by a distance of 1 mm, which is contained inside a container with inert gas at low pressure will lead to creating of a direct current at 50-100 A, causing the arc-discharge at high temperature between the poles. The use of hydrogen gas instead of inert gases such as (Ar ,He) is better to obtaining MWCNTs [14].



Fig.(1-5): Schematic diagram showing the arc discharge method [15].

#### **1.3.2.** Laser ablation method

The CNTs utilizing laser ablation was initially testified by Guo et al. (1995). Such method was an encouraging way for the MWCNT and SWCNT production. Figure (1-6) represents a schematic diagram of laser ablation. Further, this method's graphite target is vaporized by pulsed laser in a reactor of high temperature with an inflow of inert gas into the respective chamber. The inclusion of water cooled surface in the system assist in forming the nanotubes. Furthermore, Richard Smalley & co-workers utilized a graphite composite and particles of metal catalysts as well (the finest harvest was made from nickel mixture and cobalt) for the synthesis SWCNTs. Generally, this is more exclusive in comparison to the chemical vapor deposition and arc discharge[14].



Fig.(1-6): Schematic of laser ablation [14].

#### **1.3.3.** Chemical vapor deposition CVD

This technique is able to control the direction of growth on substrate and huge quantity of nanotube production as well [16]. The above mentioned techniques presented two intricate problems for example, the understanding of both the ordered synthesis and large scale production [17]. The CVD is extensive and finest method used in the synthesis of CNTs . The CVD's method required tube furnace with tube quartz, sources of carbon such as: acetylene, methane or ethylene and gas flow to carry the steam particles into the chamber shown in Figure(1-7).



Fig.(1-7): Schematic of thermal CVD [14].

There are two basic steps: First, the catalyst is a metal particle such as ferrocene and others, prepared in several ways such as (PVD: physical vapor deposition, sputtering and dip coating etc.). In the secondary step, the substance is heated up in a gaseous environment which is rich in carbon. Furthermore, the decayed carbons are immersed in catalyst through diffusion transformed for CNTs. Comparing with two methods, CVD is considered as a common economic technique for CNTs production at comparatively ambient pressure, low temperature but then at the crystallinity cost.

Being adaptable procedure, the hydrocarbon's in gas, solid and liquid state while enabling the usage of several substrates and allowing the growth of CNT in different forms .The forms may entangled or aligned, thick or thin films, coiled or straight or even an anticipated nanotube's construction at already defined sites on a patterned substrate. The two major advantages of this procedure, attainment of nanotubes is done at greatly less temperature though at lower quality. The catalyst can be placed over a substrate that permitted the CNTs for adoption of well-disciplined structures[14] .The carbon nanotube growth method is complex and still unclear and would be elaborated in the next section in detail.

#### 1.3.4. Mechanism of Growth CNTs into CVD

The nature of CNTs surface influence the properties due to growth many groups such branches or outside the wall like distortion which causing change in hybridization of carbon groups from sp to sp<sup>2</sup>. Some of changes or distortions were favored in some applications while another applications had to used specific types of CNTs [18]. As mentions before many attempts were done towards prepare a specific type by choose the method and the conditions of precipitation which mostly succeeded to make control for preparation.

The control may preparation done by many parameters such as flow rate of gas, temperature of precipitation and carrier gas. All the parameters influence in degradation of carbon source and the nature of building free radicals. This section includes an explanation of the supposed growth mechanism of carbon nanotubes to understand the ways of forming tubular structure.

Generally the mechanism depend on tow conditions temperature of dissociation and temperature of precipitation. The process include two reactions. The first decomposed of hydrocarbons than emits heat into the catalyst while the second, condensation or precipitation the carbon fragments which deposited process that emits heat [19]. The most reported literatures concerned with two properties for growth which are Tip and Base Growth, as represent in Figure(1-8). From Figure(1-8a) shows the tip

probabilities, when the catalyst has a sharp contact angle or week interactions with the substrate, causing move the catalyst on the tubes and that limited from growth large filaments. When the catalyst is connected at obtuse angle having a substrate or communication amongst strongest support and catalyst, that causing note in this pattern the failure of the carbon nanotube in pushing the catalyst to the top as shown in Figure (1-8b) [20, 21].

Mostly, this type accrues when the lack of interaction of carbon with the substrate, which leads to the avoidance of it and take carbon nanotube for the catalyst as a base for the growth of roots with more length as compare with tip growth. The greatest suitable growth molecular model of CNTs depend on forming intermediates free radical fragment refers to the progress round a point of fixed center [22]. The conjugation with sp2 carbon atoms hybridization is accountable to increase a stabilized and building tubular structures for mono or poly sheets of free radicals which produced under the high temperature [23]. Mostly the nature of sp2 hybridization which characterized by  $\pi$  bonding responsible to forming dio trio or multi-layers of CNTs.

The decomposition or degradation for the sources of carbon such hydrocarbon materials CxHyOz produce carbon fragments of free radicals as shown below:

$$Hh Cc Oo + heat \rightarrow c C^* + h H^* + o O^* - (1-1)$$

The primary fragments carbon free radicals C\* which may mono or dio or more species of free radical [24].



Fig.(1-8): Schematic representation of the two typical CNT growth modes, (a) tip growth mode and (b) base growth mode CNT [21].

#### **1.4. Literature Review of CNT**

**In 2009, S. Esconjauregui et al.,** were synthesized CNTs and various other Nano morphologies of carbon while utilizing "atypical" (Pt, Pd, Al, Mg, In, Na, Cs, W, K, Ni3C, Ir, Mn, Ti and Mo) and "typical" (Fe, Co and Ni) catalysts by chemical vapor deposition. The metal's catalytic activity intensely relies upon its electronic structure [25].

In 2009, M. Bystrzejewski et al., they studied in detail the synthesis of carbon nanotubes by CVD using eight aliphatic alcohols (methanol to decanol). it was found that the pyrolysis of alcohols comprised one to six carbon atoms in chain resulted in products containing single- and multi-walled nanotubes. Pyrolysis of C6–C10 alcohols yielded multi-walled nanotubes and carbon encapsulates filled with catalyst particles. The results show that CNTs can be synthesized in high yield from low-cost starting materials and by using simple CVD techniques [26].

**In 2010, A. Szabó et al.**, they discussed the main three methods of synthesis are; the chemical vapor deposition (CVD), laser ablation and arc discharge. Thus, the outcomes of several methods indicated in this review appears the CVD method as finest one for the MWNTs' production on larger scale [27].

**In 2010, J. Sengupta et al.,** studied the influence of Ni and Fe catalyst's synthesis on the CNTs at (APCVD) atmospheric pressure chemical vapor deposition. experimently Fe as catalyst was show best graphitization degree for CNT structure. Moreover, the mechanism of tip growth mostly causes the growth of CNTs along with Ni and Fe catalysts. The Ni-CNT was observed to be bamboo like, however, Fe-CNT emerged as metal filled straight tubes [28].

In 2011, A. Firouzi et al., succeed to synthesized CNTs is carried out on quartz substrate through (FC-CVD) at the temperature of 950°C while

utilizing the gas of methane at 150 (SCCM) flow rate and applied as gas sensors. After this, the measurement of CNT's electrical resistance is done by sensor exposure to the concentrations of  $CH_4$  and  $CO_2$  while functioning at the room temperature. Outcomes showed that sensors vastly responded to the molecules of gases [29].

**In 2011**, **Abu-Abdeen**, **Mohammad**, **and Abdu Aljaafari** , synthesized CNTs using the ACCVD method is per-formed as a function of growth temperature and at constant growth time, alcohol flow rate, catalyst concentration and carbon source. Mixture of multi-walled carbon nanotubes and carbon nanopowder is achieved at a growth temperature of 700°C. Bundles of single walled carbon nanotubes with a little multi-walled ones are grown at 800°C. A majority of multi-walled nanotubes and little bundles of single walled CNTs are grown at temperature of 900°C [30].

**In 2012, A.Aqel et al.,** discussed Carbon nanotubes in terms of history, types, structure, synthesis and characterisation methods Carbon nanotubes have attracted the fancy of many scientists worldwide .Carbon nanotubes have attracted the fancy of many scientists worldwide [31].

In 2012, M. Lubej et al., discussed the CVD method for the synthesis of carbon nanotubes, and has reviewed some theories and simulations that have been put forward to model these processes. It seems that progress is being made in simulating the nucleation, growth and termination mechanisms involved. Although the simulations of carbon nanotube synthesis differ in several respects, it appears that the main elements applied in simulations are similar. For better and more accurate numerical simulations of carbon nanotubes synthesis based on the transport and kinetics in the chemical vapor deposition reactor, a simpler system [32].

In 2013, D. Lukowiec et al., prepared MWCNT's by CVD on the substrate of silicon while comprising a catalyst having two layers of buffers and a thin film at 750°C temperature utilizing ( $C_2H_4$ ) as a source of carbon

for 45 min. they have confirmed the homogeneity, high quality and purity of the manufactured carbon nanotubes [33].

In 2013, E. G. Ordoñez-Casanova et al., used technique of spray pyrolysis, ferrocene as catalyst whereas, aliphatic alcohols such as butanol, ethanol, propanol and methanol are used as a source of carbon. Thus, this research of synthesized carbon Nanotubes illustrated significant variances in Nanotubes forming layers' number, quality & quantity as well as length diameter as per function of carbon numbers used in alcohols [34].

In 2013, Khorrami, S. A. and R. Lotfi, reported that TCVD were grown CNTs on copper catalyst with using  $H_2$  and  $N_2$  mixture. The results with TCVD were shown different morphologies when using different value of flow rate for carrier gas. The amounts of deposited carbon and length were decrease with increasing flow rates [35].

**In 2014, R. Purohita et al.**, have successfully minimized the distribution diameter of SWCNTs up to an approximate degree. They developed suitable separation processes to separate the CNTs to the semiconducting or metallic nanotubes of precise chirality. The 3 to 6 walled thin FWCNTs production is an excellent choice in comparison with thick MWCNTs, using CVD, arc-discharge and ablation laser [14].

**In 2015, Y. Li et al.**, have successfully synthesized VACNT arrays with a rapid growth rate by ethanol-assisted CVD method using a two zone

growth strategy, separating carbon feedstock pyrolysis and CNT deposition. The use of ethanol as an additive in the reaction environment, the use of two temperature zones, and the uniformity of catalyst nanoparticles were important factors contributing to the sustained and efficient growth of VACNT arrays. Both 0.8-nm- and 3-nm-thick Fe catalyst films worked well for the production of VACNT and forests of 7 mm in height could be easily obtained within 45 min [36].

In 2015, R. Sharma1 et al., manufactured MWCNT by CVD decomposition and arc discharge. The synthesis of multi-walled CNTs is done on the thin nickel film popped on a substrate of silicon with the help of de-positioning of acetylene's thermal chemical vapors at 750°C temperature. Moreover, the arc manufactured CNTs are categorized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The comparison of outcomes with grown nanotubes is carried out with the process of chemical vapor deposition [37].

In 2015, F. G. Granados-Martínez et al., produced the CNTs by CVD from hexane, butanol, ethyl acetate and diethyl ether. For the altered precursors, the temperature range for the synthesis of CNTs was observed to be of 680-850 °C. However, the diameter of CNTs from butanol was 55-230 nm, ethyl acetate was 100-300nm, diethyl ether's was 45-200 nm, while hexane range from50-130nm. The content of carbon for all samples was observed to be greater 93% and carbon nanotubes from butanol indicated 99% of carbon continent [38].

In 2016, Pandey, P. and Dahiya, M., presented several interesting properties, such as high aspect-ratio, ultra-light weight, strength, high thermal conductivity and electronic properties ranging from metallic to semiconducting. The production of carbon nanotubes can be done by plasma based synthesis method or arc discharge evaporation method, laser ablation method, thermal synthesis process, chemical vapor deposition and by plasma-enhanced chemical vapor deposition. The CNTs are valuable in the field of drug delivery, blood cancer, breast cancer, brain cancer, liver cancer, cervical cancer, gene therapy. This review leads to a useful knowledge related to general overview, types, preparation methods and applications of CNTs. [39].

**In 2017, F. Abdulrazzak et al.,** synthesized FWCNTs using homemade movable tube furnace reactor through chemical vapor deposition at 450°C and 750°C. The mixture of propanol and methanol is used as a carbon source on the caver of silica surface. This process prospered to create FWNT 450°C that had greater surface area and larger active site as compared to the FWCNT 750°C in the properties of adsorption [40].

**In 2017, N. Tripathi et al.**, used a plant derivative green catalyst which is an inexpensive synthesized for multi-walled carbon nanotubes' synthesis. The noteworthy points of this growth should be stated as: (1) all the grown CNTs are devoid of lethal metal catalysts (2) the essential lower temperature of growth (575°C) is prerequisite and manufactured high crop in relation to other catalysts utilized is being testified [41].

In 2017, Mirabootalebi, S. O. and Akbari, G., Among of the main methods for synthesizing carbon nanotubes, CVD due to simplicity, controllable mechanism, high ability for synthesizing aligned CNT, variety modified types for producing different kind of CNT, high efficiency close to 100% and suitable for mass producing; is the most attractive way for synthesis of carbon nanotubes. Laser ablation and Arc discharge are common method for synthesis CNT that both of them are not suitable for mass production, besides that; quality of yields in arc discharge is low. The problem of mass production also exists for electrolysis, and this method used in laboratory scale. In mechanic thermal despite simplicity and large scale of production, not continuous and process is very slow [42].

**In 2018, Y. M. Manawi et al.**, summarized the numerous CNTs synthesis through the method of (CVD). The carbon nanomaterials comprised of graphene, carbon Nano-onion (CNO), carbon nanotubes (CNTs), carbide derived carbon (CDC) and carbon nanofibers (CNF). Additionally, the recent challenges in the nanomaterial's application and synthesis are emphasized with recommended areas for forthcoming investigations [43].

**In 2018, Ameneh A. et al.,** they using CVD to grow CNTs at a large scale under different condition .The flow rates of 1500 sccm of Ar and 40-45 sccm of acetylene at 750°C were the optimal conditions for large scale production of nearly pure CNTs [44].

In 2019, S. Shukrullah et al., studied the production of multi-walled CNT bundles by  $Fe_2O_3$  catalyst supported by alumina with the aid of FC-CVD technique which is floating catalyst chemical vapor deposition. The molecules of ethylene were decayed in a reactor of FC-CVD for various quantities of metal nanoparticles [45].

In 2020, Liyu Dong et al., were synthesized Double-walled carbon nanotubes and continuously collected using FC-CVD method , they included de-ionized water in the catalyst system, which achieved a more uniform and controlled distribution for efficient DWCNT production. Using a water-assisted FC-CVD process with optimized conditions, a transition from multi- to double-walled CNTs was observed with a decrease in diameters from 19–23nm to 10–15nm [46].

#### **1.5.** Aim of the Research

The objectives of this work include the following items:

- **1-** Synthesis and identification with physical studies for synthesis CNTs from alcohol mixture in CVD.
- **2-** Find the best ratios of methanol/Butanol to prepare the best quantities and qualities of CNTs.
- **3-** Using synthesized CNTs in two applications solar cell and gas sensor.
- **4-** Trying to reach the best sensitivity for synthesis CNTs by changing the ratios of precursor Methanol and Butanol.
- **5-**Starting the broad strategy to synthesis and enhance the physiochemical properties of CNTs to use it in many applications with best results.



#### 2.1. Carbon nanotubes

Carbon Nanotube (CNT) is tubular form of carbon with diameter as small as 1nm and length of few nm to microns. CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube. Depending on the atomic arrangement of the carbon atoms making up the nanotube , the electronic properties can be metallic or semiconducting in nature, making them widely used in several applications due to their unique electrical, mechanical, optical, thermal and other properties. The possible applications of CNTs include conductive films, solar cells, fuel cells, supercapacitors, transistors, memories, displays, separation membranes and filters, purification systems, sensors, clothes etc.

carbon nanotubes have many characterizations such as:

- ♦ CNT is 100 times stronger than stainless steel and six times lighter.
- CNT is as hard as diamond and its thermal capacity is twice that of pure diamond.
- CNT's current-carrying capacity is 1000 times higher than that of copper.
- ✤ CNT is thermally stable up to 4000K..
- CNT can be metallic or semiconducting, depending on their diameter and chirality.

However, it is important to note that all those superlative properties were predicted for an atomically-perfect ideal CNT which is far from the CNTs we are practically producing today. Despite a huge progress in CNT research over the years, we are still unable to produce CNTs of welldefined properties in large quantities by a cost-effective technique. The root cause of this problem is the lack of proper understanding of the CNT growth mechanism. There are several questions at the growth level
awaiting concrete answer. Till date no CNT growth method could be robustly established [14].

### 2.2. Structure of Carbon Nanotubes

These are referred to the material which is one dimensional while comprising the atoms of carbon bonded forming  $sp^2$  hybridization on graphite or graphene sheet strictly associated to the arrangement of honey comb or even to the hexagons' network formed by carbon atoms. As stated in the section of re-hybridization, an extended system of  $\pi$  is formed on the p orbital of carbon atoms which permits the conduction of graphite lattice. The simplest carbon nanotube images can be perceived as a rolled up graphene sheet for the formation of seamless cylinder having a hollow core, that might close or open from both ends for instance, fullerenes[47-49].

The properties may acts as a semiconductor or metal on the base 0f diameter of tube, the helicity and wrap's direction. The Multi- wall carbon nanotubes (MWCNTs) were comprises of several coaxially organized graphene sheets layers while being rolled in a cylinder, a novel CNT type is observed termed as few walled carbon nanotubes (FWCNTs) [50], which is an exceptional MWNT type comprising of two to six graphene sheets' layers while having a precision related to the single walled carbon nanotubes (SWCNTs) structurally. Moreover, these are deliberated as a midway structure among MWCNTs and SWCNTs as shown in Figure (2-1). These are having a diameter in nanometer rang of 0.3 to 100 nanometer [49] while, reaching the length up to numerous cm. Therefore, for SWNTs, the recorded length of about 18cm was attained [51] . The diameter of distinctive SWNT was measured about 1nm while, for MWNTs, it might extend to 10nm, however, for FWNTs, these diameters were observed to be near 4-7nanometer [49].



Fig.(2-1): Structure of Carbon Nanotubes , (a) SWCNT , (b) MWCNT [52].

## 2.3. Types of Carbon Nanotubes (CNTs):

The grouping of carbon nanotubes is usually done conferring to the atomic structure in side-walls and number of the side-walls [53], namely as show in Figure(2-2):

- Single walled carbon nanotubes (SWCNTs): consists of one sheet one layer of graphene [54], with diameter 0.7-2.5 nm.
- Double-walled carbon nanotubes (DWCNTs): comprise of two carbon atoms sheets (two layer of graphene), and that flopped with each other, with diameter 1.3-5 nm.
  - Few walled carbon nanotubes (FWCNTs): have 2-6 sheets of carbon atoms (one layer of graphene).

- Multiple walled carbon nanotubes (MWCNTs): involve numerous coaxial cylinders and every single of them is formed of single sheet of graphene around a hollow core (Many layers of graphene sheet are wrapped around), "synthetic graphite in tubular shape". With diameter 4- 150 nm [8,53].
- Nanotorus: A nanotorus is a hypothetically termed as bent carbon nanotubes into torus or donut shaped form. Moreover, a nanotori consists of several distinctive properties for example magnetic moments are thousands times greater as compared to that of formerly estimated for several precise radii.
- Nanobuds: The nanobuds of carbon are freshly revealed material that combines to the already discovered carbon allotropes: carbon fullerenes and nanotubes. Such novel material of fullerene type buds are bonded covalently to the underlying carbon nanotubes' sidewalls outwardly.

Some literatures [53-56] reported that carbon nanotubes could be include some types which are sub-types as mentions below:

- Herring-bone carbon nanotubes (HBCNT): have internal structures in between the tube sidewalls
- Bamboo carbon nanotubes (BBCNT): have internal structures in between the tube sidewalls
- Cup-stacked carbon nanotubes (CSCNT): are composed by stacks of open-ended cups or cones.

All of the types which mentions before may be rolled up graphene sheets, open-ended seamless tubes, regular close-ended seamless tubes and stacked seamless cones or cups with one or more concentric layers.



Fig.(2-2): Types of carbon nanotubes.

## 2.3.1. Types on the basis of chirality

Mostly, Chirality is direct indicators for determining the electrical properties of CNTs, however many literatures were specified in this section. Briefly, the graphene sheet can be rolled-up to form three types of chirality when the orientations of groups decided the types which are: chiral, armchair, and zigzag [10] as shown in Figure(2-3).



Fig.(2-3): a. Geometries of CNT, b. armChair, c. Zig Zig, d. chair[57,58].

The design depends on the graphene sheets wrapped into a cylinder structures, the chiral vector can represent by equations (2-1),

$$C_h = na1 + na2 \equiv (n,m)$$
 ------ (2-1)

When: a1 and a2 refers to coefficient of vector on the graphene surface along the axis n and m [52]. The physical and chemical properties of tubes with verities types SWCNTs, DWCNTs, FWCNTs, and MWCNT influence directly with the angle of flopping or rolling the sheets. The equations that responsible were include the cosine relations of factor as represent by equation (2-2). The equations depend on n and m value which to accumulation value shows the physical and chemical behavior of CNTs.

$$\cos\theta = (2n + m)/(2*\sqrt{(n^2 + m^2 + n^*m)}) - (2-2)$$

where:  $\cos\theta$  is Chiral angle [52], however, the relationship between chiral angle with n and m produce three categories, thus When (m=0), with angle ( $\theta=0^{0}$ ) the nanotubes have a Zig-zag with metallic behavior. The other appears when (n=m), within ( $\theta=30^{0}$ ) which is an Armchair and appeared metallic properties while the last type chiral can occur when (n $\neq$  m $\neq$  0), for angle  $\theta$  between  $0^{0}$  and  $30^{0}$ , which may metallic or semiconductors properties [59].

## 2.3.2. Classification by Conductivity

Carbon nanotubes may behave as metallic and semiconducting nanotubes that are majorly impacted by the CNT's chirality [51], while determining the various chirality by values of m & n. Moreover, there is a mathematical possibility to establish the carbon nanotubes categories giving two possibilities; the 1<sup>st</sup> probability is due to the n-m being a multiple of 3 or an armchair and after that the nanotube becomes metallic. The 2<sup>nd</sup> denotes to the n-m when these are not the multiple of 3 or chiral or a zigzag, in this case a nanotube becomes a semiconductor.

### 2.4. Defects of CNTs

During the process of synthesis MWCNT there are many defects in internal and external tubes, mostly can be related to stress induced or production process, and can be divided into[60]:

- 1- Geometrical and topological mostly accrued with the SWCNTs.
- **2-** The sp<sup>2</sup> converted to sp<sup>3</sup> for a C–C bond due to highly localized will produce re-hybridization defects.
- **3-** Defective bonding and other defects, such as Vacancies, contamination attachments and substitutions.

The three types of defect commonly accrued which shown due to the causes below [61]:

**1-Doping defect**: this type were refer to replace one or several carbon atoms on lattice structure within another atoms such  $N_2$  or S as shown in Figure (2-4) which commonly exist in both single and multi-wall carbon nanotubes.



Fig.(2-4): (color online) Doping defects [62].

**2- The Stone–Wales Defect**: or it could be called 7557 which means the transfer from hepta to penta than ending with hepta orientations as shown in Figure (2-5). However mostly causing change on crystallographic and topological of CNTs.



Fig.(2-5): The S-W formation in the hexagonal lattice of CNTs: (a) pristine lattice and (b) SW-defected lattice[60].

**3-Vacancy Defect** : the defect was accorded when re-hybridization for two of the surrounding three dangling bonds which caused link with each other to create a shape of pentagon as indicated in Figure (2-6).



Fig.(2-6): Atomic vacancies present on outer walled of DWCNT [60].

### 2.5. Carbon Nanotubes Properties

properties of carbon nanotubes are fully benefited with CNT's thermal & electrical conductivity, mechanical strength and aspect ratio. In this section we explain some of this properties

## 2.5.1. Electrical Conductivity

The conductivity of CNTs has been indicated as a degree of twist, function of their chirality and their tubular structure's diameter. A metallic CNT could be deliberated as a material with high conductivity, Moreover, chirality which is termed as a graphene sheet's twist degree regulates the CNT interconnects conductivity. The indices of chirality, CNTs demonstrates both semiconducting and metallic properties, furthermore the MWCNTs' electrical conductivity is relatively intricate as their interactions in inter-wall do not equally dispense the current over a single tube [62].

#### 2.5.2. Strength And Elasticity

Being a single graphite sheet, each carbon atom is associated to the three neighboring atoms through a strong chemical bond. Therefore, CNTs display a sturdiest elastic modulus of basal plane and henceforth, are considered to be a definitive a fiber of high strength. The SWCNTs' elastic modulus is considerably higher as compared to the steel which makes them greatly resilient. However, pressing the nanotube tip will bend it but with the removal of force , the nanotube will return back to its original state. Thus, this CNTs property turns them to be enormously valuable as the tips of probe for high resolution scanning probe microscopy[63].

### 2.5.3. Thermal Conductivity And Expansion

Because of the strong graphene in-plane C-C bonds, the CNTs reveal superconductivity under 20K roughly about 253 °C. These strong C-C bonds offers a remarkable strength & stiffness compared to the axial strains. Additionally, the SWNTs' zero in-plane and greater inter plane thermal expansion causes a higher flexibility contrary to the non-axial strains. Furthermore, the larger in-plane expansion and high thermal conductivity of CNTs demonstrates thrilling projections in nano-scale molecular electronics, strengthening the functional composite material's additive fibers and also in actuating or sensing the devices. The current measurements of experiment recommend that matrices embedded with CNT are much stronger than that of the bare matrices of polymer (Wei et al. 2002). Thus, it is estimated that nanotube might also considerably progress the thermal and thermos-mechanical properties of the composite resources[63].

# 2.6. Overview of CNT Characterization Methods

Several attractive physico-chemical characteristics[64-66] have turned the CNT as a significant material for the applications of broad spectrum. To distinguish morphological, structural and physico-chemical features, numerous techniques such, Raman spectroscopy, Energy dispersive X-ray diffraction, XDR, Field Emission Scanning Electron Microscopy, and Transmission Electron Microscopy have been suggested, however, no technique is present which can probe all the features of the CNT.

## 2.7. Raman Spectroscopy

Figure(2-7) shows the photograph of the instrument. The innovatory progress in instrumentation had led the Raman spectroscope to be more influential investigative tool used for the evaluation and characterization of great variety of materials for many applications. Mostly this techniques can comprise of the structural component investigation, crystallographic orientation, electronic devices inorganic or organic thin film and mechanical stresses without any limitations.

In this procedure, the line of Raman spectral are attained through a sample illumination with a potent infrared laser source or a source of visible monochromatic light. Moreover, a hybrid technique amongst the microscopy and Raman spectroscopy is termed as a Raman microscopy. Hence, this technique is utilized to keep the Raman maps record while utilizing a process of point mapping just to signify the spatial dispersion of various chemical components.



Fig.(2-7): The photograph of Raman spectroscopy.

### 2.7.1. Basic Principles and Instrumentation

The encroachment of monochromatic light on a molecule occurs which lead to the inelastic and elastic scatterings that are being presented as significant scattering procedures. The occurrence of inelastic scattering is due to the alteration in photon energy while elastic scattering happens because no variation in photon energy. Therefore, three categories of the scattering phenomenon can be exhibited in Figure( 2-8).

**First**; having an identical frequency and wavelength of the scattered light as that of the incident photon turns the procedure to be elastic in nature as the loss of energy is insignificant termed this phenomenon as a Rayleigh scattering method. A minor section of the elastically scattered photons happens because shift the frequency. Therefore, the incident photon frequency through the quantity of vibrational energy gained or lost by a molecules is acknowledged as a Raman scattering.

**Second**; the attainment of the vibrational energy from incident photons for molecules terms the scattering as a Stokes Raman Scattering. This represents the scattered photon's energy would be less than the incident photons energy.

**Third**; losing a molecules' vibrational energy to the incident photon terms the scattering as anti-Stokes Raman scattering, in which the scattered photon's energy would be greater than that of the incident photons. the higher incidence probability, Stokes Raman Scattering is utmost frequently utilized in molecular vibrational studies than that of the anti-Stokes Raman scattering [67].

Raman spectroscopy produces the related to the defects, tube alignment and purity. This further contributes distinctive occurrence of MWCNTs compared to the other allotropes of carbon. This procedure has been amazingly effective to describe the SWCNTs' structural properties [68].

The Raman spectrum of CNTs can be categorized into three distinguishable features: the high energy mode (HEM), D mode and radial breathing mode (RBM). Each of these features demonstrates different properties of SWCNTs, with two dominant features appear in every Raman spectra of CNT samples [69]. Presently, the indication in Figures (2-8) and (2-9) assists in evaluating the approximate key annotations for each concerned region to the CNT Raman spectra .



Fig.(2-8): The diagram showing the type of transition of the electrons and the Rayleigh and Raman scattering[70].



Fig.(2-9): Raman Spectrum of SWCNT, DWCNT and MWCNT samples[71].

## 2.7.2. Radial Breathing Mode (RBM)

The mode of radial breathing is normally observed in a range of 100-300 cm<sup>-1</sup>, these bands signify shows difference between SWCNTs and other forms of carbon since these components are not observed in any other sp<sup>2</sup> bonded carbon material. The in-phase symmetric dispositions of entire carbon atoms nearby the tube, which provides some indication of the diameters in the sample, and also identifies whether the tubes are multi or single-walled. In MWNTs, the RBM band can be seen if the inner tube diameters are very small (less than 5nm usually). Moreover, the RBM band's frequency ( $\omega_{RBM}$ ) relies upon the tube's diameter which can be articulated by:

$$\omega_{\text{RBM}} = A/d + B$$
 ------ (2-3)

when, d represents the tube's diameter, A is a proportionality constant, and B is a damping variable caused by the environment around the tube. Which mostly zero for tube, B is expected to be zero[72-74] .Whereas, the outer curvature sheet of MWCNT is adjacent to the graphene while, inner sheets being identical to SW-carbon Nanotubes. Conversely, the innermost shell's diameter considerably relies on the procedure's sensitivity which has been utilized for the development.

### 2.7.3. The G-band

The double peak structure, referred to earlier, is associated with the G-band, tangential vibrational modes of the CNTs, which is associated with the Raman graphite spectra. The G band in CNT's is due to the curvature of the graphene sheet and is split into two peaks: G<sup>-</sup> peak and G<sup>+</sup> peak. The G<sup>-</sup> peak has a lower frequency which is more visible in semiconducting tubes, as in metallic tube samples it also has a lower intensity and is much broader, making it less visible. The G<sup>+</sup> peak is higher frequency and has no significant difference in frequency or width between metallic and semiconducting tubes [73-75]. In samples of MWNTs where a large portion are metallic, the G-band is visible as a single peak. The D-band is found at frequencies between 1250 and 1450 cm<sup>-1</sup>, while its overtone appears at approximately double the frequency ranging between 2500 and 2900 cm<sup>-1</sup>.

### 2.7.4. The D-band

D-band is generally termed as defect band due to the D band's intensity which is relative to the tube's number of defects. The D bands' estimated intensity & width can be utilized for determining the graphitic material's fraction existing in the sample material [73-75]. A common quality idea of grown nanotubes can be attained measuring the D & G bands' ratios. The D band's intensity can be used to oversee damage being

inflicted on the sample from various processes used in its purification, such as tip sonication or centrifugation. Gohil and Ghosh observed the MWCNT Raman spectra placed over an active substrate of SERS (surface enhanced Raman scattering) and verified the tangential mode's (G-band) multiple splitting occurrence. Likewise, the splitting of D band induced by a disorder into distinctive features which are absent at room temperature otherwise [76]. Moreover, the D-band splitting (~1350 cm<sup>-1</sup>) observations designated the double resonance conditions fulfilled for the MWCNTs which had been deposited on the active substrates of SERS at lower temperatures.

To utilize the Raman spectroscopy for purity assessment by distinctive methodologies depend on the G-band peak and D-band peak's intensity ratio. Moreover, the D band represents a double resonance peak induced by a defect happens because of the elastic scattering through defect and inelastic scattering via a phonon. Henceforth, the unorganized samples should demonstrate a higher intensities for D band integrated intensity ratio to the G band ( $I_D/I_G$ ) which is an upright indicator for the quality of sample [77-80].

## 2.8. XRD Application in CNT Characterization

#### **2.8.1. XRD Fundamental Principle**

X-Ray Diffraction (XRD) is one of the major techniques utilized for solid-state materials' characterization. X-ray diffraction patterns provide information with respect to the crystallinity of a material and the average crystallite size. Typically, the materials are formed of identical atomic planes' repeating units that generate crystals. The polychromatic X-rays are formed in a special tube acknowledged as cathode-ray tube. A monochromatic is utilized to filter the polychromatic X-rays to produce the mono-chromatic radiations of diameter  $<10 \mu m$  that can hit the atomic planes of materials. Conferring to the Bragg's law as show in equation (2-4), these incident rays interact with the atomic planes' samples which produce the scattered, transmitted, adsorbed, refracted and diffracted beams[81].

$$n\lambda = 2d\sin\theta \dots (2-4)$$

Here, *n* indicates the integer defining the diffracted beams' order, while,  $\lambda$  demonstrates the incident X-ray beam's wavelength, *d* denotes to the distance amongst d-spacing or adjacent atomic planes and  $\theta$  shows the incident X-ray's angle as show in Figure(2-10).

The diffracted X-rays' degree relies upon the arrangement of atomic planes inside the lattice of crystals. Thus, law describes the angle of diffraction and spacing of lattice atomic planes at specified electromagnetic radiation's wavelength. Normally, the diffracted X-rays are detected by a detector following the processing and counting to provide patterned or diffracted beams. Transformation of the diffracted patterns into the dspacing permits the unknown sample's identification. Usually the recognition of materials is done by relating the reference patterns that are generally present in the library of JCPDS (Joint Committee on Powder Diffraction Standards) with diffracted patterns.[81,82].



Fig.(2-10): Schematic to derivate the Bragg's Law X-ray (arrows) are reflected by crystallographic planes separated by a distance (d) [82].

### 2.8.2. XRD Experiments for CNTs

The XRD examination's principle for CNTs have been depicted in Figure (2-11). The monochromatic beam of X-ray is fixated on the material of sample to solve the hidden structural info inside the crystals. Though, being deliberated as a non-crystalline material, the periodic structure of the CNT forms distinctive peaks of X-ray diffraction[83] Moreover, XRD has been effectively used to inform about the CNT's structural and morphological features which have been associated to various angles [84-87].

The carbon nanotube's and carbon atoms performs as a 3D optical diffracts scatter the light at altered yet specified angle, Thus, it is

conceivable from the diffracted angles to take out the information on the CNTs' graphene aligning sheets form the diffracted beams' intensity and positioning [88]. Further, the XRD pattern has indicated several discrete resemblances to the graphite perhaps due to their identical properties of intrinsic graphene [89].

The lattice plane is present more specifically 001 which turns the peaks of the diffraction pattern specified and altered form carbon based crystals of  $sp^2$  [90]. Additionally, due to the CNTs' cylindrical and curvature structural shapes, the carbon atoms' dipole moment can be altered in the 2D graphite direction. Investigation of dipole moment's direction or the nanotube structure's atomic dipole vector can assist in CNTs' characterization and give graphite and CNTs' differentiating points.

The peak of CNT diffraction intensities relies on the morphological orientations of CNTs. Striking the single walled CNT by X-ray beam, a 002 peaks have several (h k 1) parallel reflections are produced. The passage of the X-ray beams through a hollow CNTs' central core, roughly some hexagonal peaks arrays such as (h k 0) are produced. There is a possibility that this might happen several times at various azimuths while being dependent on the existing helix number.[91,81].



Fig.(2-11): Schematic diagram of basic principle of XRD for CNT [81].

# 2.9. Structural Parameters:

## **2.9.1.** Lattice constants (*a*, c) of tetragonal structure

The lattice constants for the Hexagonal structure can be calculated according to the following equation (2-5) [92]:

Where *hkl* are Miller indices.

## 2.9.2. Average crystallite size (Dav)

The average crystallite size (D<sub>av</sub>) can be estimated using two methods:

### a. Scherer's method

Crystallite size can be calculated from peak broadening using XRD. X-ray line broadening method was used to determine the particle size using Scherer's equation [93]:

Where K: is shape factor and was assumed to be equal to 0.9,  $\lambda$  is the wavelength of incident X-ray radiation = (1.5406 Å for CuK<sub> $\alpha$ </sub>) and  $\beta$  is the full width at half maximum of the peak (in radians).

### b. Williamson-Hall method (H.W)

Crystal imperfections and distortion of strain-induced peak broadening are related by  $S \approx \beta s$  /tan $\theta$ . Scherer's-equation follows a 1/cos $\theta$  dependency but not tan $\theta$  as the induced strain. The following results are the addition of the Scherer's equation and  $S \approx \beta s$ /tan $\theta$  [94-96].

 $\beta hk\ell = \beta D + \beta S \dots (2-7)$ 

$$\beta hk\ell = (k\lambda/\beta cos\theta) + 4Ssin\theta$$
 .....(2-8)

Where S is the microstrain. Rearranging equation (2.6) gives:

$$\beta \, hk\ell \, \cos\theta = \left(\frac{k\lambda}{\beta \cos\theta}\right) + 4Ssin\theta \dots (2-9)$$

If  $\beta$  hke cos $\theta$  is plotted with respect to 4sin $\theta$  for the peaks, strain and crystallite size can be calculated from the slope and y-intercept of the fitted line respectively [94-96].

### 2.9.3. Dislocation density and number of grains

The dislocation density ( $\delta$ ) can be calculated as the following [97]:

And number of crystallites can be calculated from the relation:

Where  $\mathbf{t}$  is the thickness and N<sub>0</sub>: is the number of crystallites

### 2.10. Scanning Electronic Microscopy SEM

An images utilizing electrons than that of light just to produce an image which would scan specimens' surface in a vacuum chamber as show in Figure(2- 12). An electron beam is fixated on the specimen's volume spot which further causes the energy transfer at that spot while eliminating the electrons from specimen, the eliminated electrons which are also termed as 2ndry electrons are fascinated, and placed together with the assistance of a detector or biased grid, finally, these are converted to single through translation. Moreover, the practicing method such system relies upon the phenomenon's number occurring on surface that already been under the electrons' effect. These are more significant to the microscope & secondary electron's discharge along with the few tens volts energy while, re-emission or electron's reflection having high energies respond the primary beam of electrons. The intensity of discharge for every secondary electron is extremely delicate as it counter offense the angle of electron beam hitting the surface area such as the sample's topographic features.

A metallic filament is heated to produce an electron's beam at the microscope top. The column repairs the path's direction straightly with the

electromagnetic lenses that concentrate and pull a line to the beam and also down to the sample's direction. The other electrons scatter back while ejecting the secondary ones from sample material. Further, the detectors gather all the backscattered and secondary electrons and transform them in a signal to view at screen just to synthesize the image from given sample in a deliberated section.

The SEM synthesized magnification is a ratio amongst the dimensions of last displayed image as well as the specimen's scanned field. Normally, SEM magnification range is among 10-200 000X while, resolving power (resolution) is amongst the 40 to 100Angstroms and 4-10 nm. FESEM or field emission scanning electron microscopy is a reformed technique that comprised of a huge activity scope in comparison to the SEM devoid of any improvements through emission by field. This is an imaging technique with high resolution giving structural and topological information in cross section or in a plain view. In the last year several instruments merged with SEM to form a more active system for investigation and sometimes in combination with SEM.

The quantitative and qualitative analysis of elements existing in SEM image's selected area is carried out by Energy Dispersive X-Ray Spectroscopy (EDS). Moreover, the collective abilities of EDS and FE-SEM permits the irradiation through a fixated beam of electrons, backscattered electrons, X-ray energy analysis or by secondary imaging. Distinctively, the applications of SEM consists of cross sectional or plain view imaging for the development of the procedure as well as for the analysis of failure. The applications of EDS consists of compositional analysis and specified analysis of defects[98-100].



Fig.(2-12): Schematic of a Scanning Electron Microscopy[99].

### 2.11. Transmission Electron Microscopy TEM

The Transmission electron microscopy (TEM) signifies to be an utmost significant prerequisite in nanotechnology science. Figure (2-13) represented a tool that can attain precisely high quality images for examining several chemical and physical properties having 100-100keV resolution. Moreover, this comprises of surface nature, magnetic, electronic properties, density and size. Further, these are chemically denoted by the bond's strength amongst the samples' components in order to alteration happened in the materials[101] after reaction processes. This procedure depends upon the electrons, where one kind of the ionizing radiations have the ability to remove the firmly bound electrons of inner shell from the nucleus' attractive field. The TEM's resolution  $\rho$  can be observed by simple equation utilization (2-12), which is also called as Abbe's theory of image creation for the beam of incoherent electrons.

$$\rho = \frac{0.61\lambda}{\sin\alpha} \quad \dots \quad (2-12)$$

As the direct impact of  $\rho$  over incident light's wavelength  $\lambda$  and angle  $\alpha$  maximum value amongst the deflected and incident beam in the lens diffusion limitation, for the wavelength's fixed ring, incident light must be concentric. It also needs a lens of greater efficiency that has found yet. Though, this issue can be lessened by utilizing several lenses just to enhance the TEM resolutions activity. Thus, the sample analyzing procedure consists of specified arrangements to organize the sample for the system of TEM. This is because of several reasons for example, the scattering which occurs due to the strong interactions amongst the sample's atoms and beam electrons. However, the sample's thickness is significant that impact the system's effectiveness while depending on the acceleration voltage, properties of materials and single analytical procedure's requirements. Thus, the test's required intensity must be adequate enough for the 100nm

electrons' transmission. Hence, there are several proceedings that handle the drawbacks which are given below:

- 1- To examine the sample's preparations, an extensive time is a prerequisite.
- 2- Merely a smaller section of the sample can be inspected.
- 3-The usage of the electron beam in such techniques can harm the samples for instance inorganic substances, biomolecules and living objects.

Kroto *et al.*[6] reported that transmission electron microscopy (TEM) represents the ideal methods for carbon nanomaterial research due to the ability of carbon atoms to form different structures such as diamond, graphite, fullerene, carbon nanofibers, and multi-walled carbon nanotubes [99,102]

Any kind of carbon nanotubes and carbon nanofibers appear to be identical upon observing through scanning electron microscope. The differentiation amongst the multi-walled carbon nanotubes and carbon nanofibers is almost difficult except perceived with TEM usage as the previous are found to be solid packed 1-D nanostructures and later ones are concentric hollow 1-D Nano tubules. Moreover, TEM provides a proper perception of carbon material's nanostructures. The interpretation of TEM can be observed to find out about the CNT wall's nature, either it is properly crystalized or not[103,104] Additionally, this gives a straight understanding of these materials' microstructure and also informs the material's form or nature as well. Furthermore, the HR-TEM (high resolution transmission electron microscopy) investigates the carbon nanofibers synthesis. Moreover, the SWNT carbon nanotubes are extremely significant in acknowledging the carbon atoms' orientation in CNTs and also to know either these are producing semiconductor or metallic ones.[104-106].



Fig.(2-13): Schematic of core components of a TEM microscope [99].

### 2.12. Optical Properties of Crystalline Semiconductors

The study of the optical properties of a material is interesting for many reasons. Firstly, the use of materials in optical applications such as interference filters, optical fibers and reflective coating requires accurate knowledge of their optical constants over a wide range of wavelengths. Secondly, the optical properties of all materials may be related to their atomic structure, electronic band structure, and electrical properties.

## 2.12.1. Absorbance (A)

Absorbance can be defined as the ratio between absorbed light intensity (I<sub>A</sub>)by material and the incident intensity of light (I<sub>0</sub>) [107]:

 $\mathbf{A} = \mathbf{I}_{A} / \mathbf{I}_{o}$  .....(2-13)

## **2.12. 2. Absorption coefficient** ( $\alpha$ )

When light proceeds from one medium into another (e.g. from air into a solid substance), some of the light radiation may be transmitted through the medium, some will be absorbed, and some will be reflected at interface between the two media. Absorption coefficient .may be defined as the decreasing ratio in incident ray energy in distance unit toward wave propagation inside the medium. Absorption coefficient is characteristic of the particular semiconductor material; furthermore, it varies with the incident photon energy (hv) and semiconductor property [98]. When incident photon energy is less than the energy gap, photon will transmit and the transmittance for thin film is given by the relation [107]:

$$T = (1-R)^2 e^{-\alpha t}$$
 .....(2-14)

Where: T: is transmittance, R: is Reflectance and t: is the thickness.

The absorption coefficient can be estimated from the absorbance using the formula[108,109] :

 $\alpha = (2.303 \times A)/t$  ..... (2-15)

# 2.12.3. Optical Energy Gap (Eg)

The term "band gap" refers to the energy difference between the top of the valence band to the bottom of the conduction band. Electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition, the band gap energy. Measuring the band gap is important in the semiconductor and nanomaterial industries. The band gap energy of insulators is high (> 4eV), but lower for semiconductors (< 3eV). The energy band gap in some semiconductors tends to decrease as the temperature is increased [111].

The energy gap for allowed direct transition materials can be estimated by plotting a graph between  $(\alpha \text{ hv})^2$  and (hv) in eV, a straight line is obtained and the extrapolation of this line to  $(\alpha hv)^2 = 0$  gives the value of the direct band gap of the material [112].

# 2.13. Some Optical Parameters

#### **2.13.1. Extinction Coefficient** (K<sub>o</sub>)

This represents the extinction occurring in the electromagnetic wave inside the material; it is also represented by the imaginary part of the complex refraction index and is related to the absorption coefficient by the following relation [107,108]:

$$K_{\rm o} = \frac{\alpha \lambda}{4\pi} - \dots - (2-16)$$

Where:

 $K_0$ : is the extinction coefficient and  $\lambda$ : is the wavelength of incident photon.

#### **2.13.2.** Dielectric Constant (ε)

When light is incident on the atoms in the material, a reaction between incident radiation and the charges of the material will happen. This will lead to a polarization of the charges of the material [108,112]. The dielectric constant can be represented by the flowing equation:

Where  $,\epsilon_1 :$  is the real part of the complex dielectric constant and  $\epsilon_2 :$  is the imaginary part of it. For the calculation of the dielectric constant in its two parts one can use the following expressions:

ε<sub>1</sub> = n<sup>2</sup> - k<sup>2</sup> • ..... (2-18)ε<sub>2</sub> = 2 k • n ..... (2-19)

#### 2.14. Nanotubes Applications

Many literatures were reported using all types of CNTs in pristine and impregnated with different materials in huge applications. In this section we reported briefly some of common applications that used in different fields such produce and storage of energy, sensor for different gases and removal the pollutants from environmental.

#### 2.14.1. Energy Storage

The anticipated fundamental characteristics of CNTs in material are utilized as capacitors, batteries' electrodes which are two hurriedly increasing significant technologies. the high surface area, CNTs have good electrical conductivity & significantly, the linear geometry of CNTs creates the surface extremely reachable for electrolytes. Several studies have indicated that CNTs possess utmost reversible any carbon material's capacity for lithium ion batteries usage[106]. Additionally, CNTs are being marketed for the application as these own exceptional materials for the supercapacitor electrodes[113].

Moreover, CNTs comprised of diverse duel cell components' applications. They consists of numerous properties such as, thermal conductivity and great surface area that turns them to be beneficial as supports of electrode catalyst in fuel cells of PEM. Due to their greater electric conductance, these might be utilized in diffusion layers of gas and current collectors as well. The toughness to weight and high strength of CNTs might also demonstrate their worth as composite component's part in fuel cells which are organized in the applications of transport indicating their enormously significant robustness.

#### 2.14.2. Gas Sensors

Gas sensor is a device that has the ability to change its physical properties for instance, mass or electrical conductivity when being exposed to the various phased chemical compounds' mixture. The alteration in properties have been perceived as an electrical indication and further utilized for the species detection. Generally, gas sensors are required to perform within required ambient and process conditions with fast response time and acceptable accuracy. They must conform to size, weight, and cost constraints of individual applications and measure the properties within the required range over an acceptable lifetime.

Gas sensors can be classified according to their operating principles as metal oxide semiconductor sensor, electrochemical sensor, gas sensitive field-effect transistors (FETs), solid electrolyte, pellistor catalytic gas detector, bulk and surface acoustic wave devices (BAW and SAW), and conducting polymer, etc. Presently, sensors of chemical gas have widespread applications in control of automobile combustion, drying & energy operations markets, monitoring of toxic & combustible gas and medical analysis. Further evolving markets comprise of automobiles, processing of beverages and food, consumers' products and wastewater treatment etc. [114-116].

The main benefits of commercially obtainable gas sensors are their function simplicity, low cost and smaller size. The measurement of size is usually done in centimeters into the micrometers while minimizing the cost by batch fabrication of larger scale. While comparing it to the various analytical instruments of conventional laboratory scale i.e. mass spectroscopy, ion mobility and gas chromatography, the devices of gas sensor property need more simple equipment for the analysis and operational cost is observed to be much lessor. Moreover, the gas sensor devices are operative in real time in situ applications.

### 2.14.3. Dye Sensitized Solar Cells (DSSCs)

Dye sensitized solar cells (DSSCs) are considered to be a solution for the problems of environment and global energy as these are low cost, clean, efficient and durable and easy to manufacture. However, raising its efficiency is still an important issue. Generation of solar cells after silicon and thin films, as the first and second generations are highly efficient but expensive. The ideal pigment cells include three basic components: a chemically adsorbed dye on the titanium nanoparticles, photolytic oxidation, reduction and conductive electrode (cathode). The principle of this type of apoptosis is as follows:-

The elevation of photosensitizers is done from ground state to that of the pigmented one.

$$D + hv - D^* - (2-20)$$

Further, the excited electrons are inserted to the semiconductor titanium electrode's conduction pack:

$$D^* - D^+ + e^- (TiO_2)$$
 injected ------ (2-21)

The injected electrons travel between accepter to the opposite electrode (cathode) during the outer-load circuit. Oxidative medium formulas  $(I^{-}/I_{3}^{-})$  that successively obtain electrified syringes on the conductive electrode

 $I_3^{-} + 2e^{-} - - - - - 3I^{-} - - - - - (2-22)$ 

Electrons are lost during oxidation of the dye and quickly replaces the ion I<sup>-1</sup> to the ion I<sub>3</sub><sup>-1</sup>, the ground state is regenerated D:

$$2D^+ + 3I^- - 2D + I_3^- - (2-23)$$

These steps get billions of times per second. Figure (2-14) shows the principle of DSSC work.

There are two main interactions to determine DSSC efficiency:

 The reaction gets to recover the electron injected by the oxidized medium before the electron crosses through the outer circuit to the conductor electrode.

 $I_3^{-} + 2e^{-} (TiO_2) ----- 3I^{-} ----- (2-24)$ 

 Second reaction represents the recombination of immersed electrons with oxidized dye:

 $D^+ + e^- (TiO_2) ----- D ----- (2-25)$ 

Figure (2-14) shows the principle of DSSC work These steps get billions of times per second [117,118].



Fig.(2-14): Structure of dye –sensitized solar cells (DSSCs) [119].



#### **3.1. Introduction**

This chapter describes mechanisms, tools and methods were worked in the present study. They are used to prepare and characterize catalysts and MWCNTs. In order to evaluate the potential manufacturing applications of CNT's, it is important to characterize the materials and understand its basic physical and chemical properties.

Besides, it is fundamental to control their properties through production, purification and modification processes by means of high quality procedures. A wide-ranging of tools agreements researchers to study CNTs, although each of these techniques reveals only a portion of the full spectrum of properties. In this chapter the techniques used during this research, are briefly described.

### **3.2. CNTs Synthesis Process**

#### **3.2.1.** Chemical Vapor Deposition Unite

Chemical vapor deposition (CVD) process consists of tube furnace equipped with quartz tube, which represent the reaction environments. The tube furnace generally include three types: mono- stage and dio-stage, that means one zone of heating while the ether include two zone of heating, mostly the second stage was higher temperature then the first stage.

The last types which used in this works include three zone, the middle zone when the precipitations were accrued was more heating temperature as compare to the ether two parts. The temperature inside the system was enough to dissociation the sources of carbon and forming the product in the center of tube which was more than 500°C.
The process of synthesis can be done without catalyst or with catalyst usually supported on a silicon wafer or quartz substrate [4,120,121]. Mostly the sources of Carbon were carry by inner gases towards CVDs system such as Ar, Ne, and N<sub>2</sub>. The process gained popularity due to its ability to grow well separated, long single wall carbon nanotubes with less defect density and amorphous carbon content, compared to processes that utilize physical route such as plasma [4].

Widely and typically acceptance in research community, several groups have focused on optimizing the CVD process. Before going into the details of this technique it will be helpful to look into various steps that define this type of growth technique. Figure(3-1) shows an overview of our experimental part to synthesized CNTs at atmosphere pressure which we could it CVDs.





# **3.3.**Chemicals and Materials

The chemical materials used in this work are listed in Table 2-1. All the used chemicals were employed without further purification.

# Table (3-1) : Chemical and Materials.

No.	Chemicals	Company supplied
1	Nitric acid (70%)	Fisher
2	Hydrogen peroxide (30%)	Barcelona-spain
3	Ferrocene [ $(C_5H_5)_2Fe$ ], 96–99% purity	Sigma
4	The glass plates fluoride doped tin oxide (FTO)	German
5	Nitrogen gas (99.999%)	Emirates industrial gases
6	Z907 Industry standard dye $(C_{42}H_{52}N_6O_4RuS_2)$	Dyesol Co.,Australia
7	Butanol (99%)	Alfa,Aesar
8	Methanol (99.85%)	Alfa,Aesar
9	Ethanol (99.93%)	Alfa, Aesar
10	Titanium dioxide powder (TiO <sub>2</sub> ) anatase (21 nm)	Evonik, Germany
11	Multi-walled carbon nanotube (95%)	Aldrich

#### **3.4.** Preparation of substrates

#### **3.4.1. Substrate cleaning**

The dimensions of quartz substrates were different shapes. The substrates were used as support the catalyst. These substrates were cleaned by labritory acetone with purities reach to 99.99% with using ultrasonic water bath at 40°C for 30 min, after that washed with deionized water before dried with dry nitrogen.

#### **3.4.2.** Catalyst Preparation

Two factors that could be critical parameter in growth CNTs with specific qualities and quantities which are size and composition For being the oriantation and number of catalyst active sites . the common materials that used as catalyst was Transition metal due to advantages of high carbon solubility, large carbon diffusion rates and high melting temperatures [122]. When the process of synthesis CNTs needed for catalyst, the first step is the preparation of catalyst , that could be done by many methods such dry impregnation method [123]. In a typical catalyst preparation, 0.5 g of Ferrocene was dissolved within 30 ml of ethanol, to get the desired amounts for preparing catalysts. The bases of the quartz were immersed in the solution and placed in a ultrasonic water bath at 40°C for 30 min, until the process of mixture and the volatile impurities to escape out, behind the Ferrocene material deposited on the bases of quartz as shown in Figure(3-2).



Fig.(3-2): The quartz sample: (a) before deposition catalyst

(b) after deposition catalyst.

#### 3.5. Carbon precursor

The CVDs techniques required in our case convert the sources of carbon from liquid to vapor phase that done by equipment unite with CVDs. The source of carbon which used in this work was include mixture with different ratios of Methanol /Butanol (C1/C4).The temperature of evaporation for all the precurers was kept constant at 80°at ATP. Although increased temperatures are required for higher rate of nanotube growth, very high temperatures can initiate self-dissociation of gases which can cause catalyst poisoning. Hence, low pressure growth has also been used to decrease catalyst poisoning

to achieve ultra-long CNTs [124] .Another important parameter associated with the precursor is flow rate of precursor. At very high temperatures where the precursor is near self-dissociation, the reaction rate gets limited by the precursor flow rate in the system. High flow rates can increase the rate of growth but just like high temperatures can also result in more of carbon soot formation and hence catalyst poisoning as seen below in Figure(3-3).



Fig.(3-3): MWCNT's as carbon soot formation on quartz sample.

#### **3.5.1.** Carrier Gas Flow

Flow rate of carrier gas  $N_2$  influence directly in the precipitation process due to providing enough time to dissociating carbon precursor which influence in the abilities to build the tubular structure. In addition to affecting reaction rates, gas flow conditions are also responsible in defining CNT length and orientations during growth. A recent publications on suspended growth of nanotubes found local thermal oscillations to play a critical role in obtaining aligned growth[125]. In our work, we used rate flow of N<sub>2</sub> as carrier gas at 125 cm<sup>3</sup>/min which responsible to achieve best precipitation rate.

## 3.5.2. Time of Growth

Growth time was also considered as an important parameter in CNT synthesis and its effect on CNT growth in order to understand growth mechanism of CNTs [126]. In this work, growth times were established at 30 minutes onto  $25 \text{ cm}^2$  on surface area of support with catalyst.

## 3.5.3. Growth Temperature

The ideal temperature for CNT growth depends on several factors, mainly carbon feedstock, catalyst, and the type of CNTs desired (single or multi wall). Nanotubes are typically grown in a temperature range from  $550^{\circ}$ C to  $1000^{\circ}$ C [127] with CVDs. In addition to the changing of the reaction kinetics during growth, the temperature plays an important role in the pre-growth treatment of the catalyst. Small catalytic nanoparticles readily oxidize under ambient conditions ; therefore, to bring them back to native state, thus mostly a controlled reduction step is required at moderate temperatures (~700°C) [8].

# **3.5.4.** Setting of the Tube Furnace

In this work we used the tube furnace Contains three heat zones obtained from Nabertherm, USA. Put in it quartz tube having a diameter of 3cm with length 120 cm, Figure(3-4) shows the furnace tube which used in this work.



**Fig.(3-4): (a) the furnace which is used in this work** 

(b) schematic of the growth temperature.

### 3.6. Experimental details in CVD

In the CVD synthesis of the CNTs, the first step is the doping of catalyst on the support surface as we reported previously. The as-prepared catalyst was put in a quartz boat distributed evenly and placed in the center of CVD furnace. The growth of the CNTs in the furnace was accrued in fourth steps. At first step N<sub>2</sub> flow rate was (200 sccm) was passed into the furnace than reduce to 125 cm<sup>3</sup>/min, when reach to 700° C with speed of heating  $3.5^{\circ}$ C/ min after that heating the source of carbon for evaporation temperature for 30 min. finally reduce the flow of N<sub>2</sub> to 50 cm<sup>3</sup>/min until reaching room temperature.

In this work ,we used The CVD system include the following components : (1) Tube furnace with diameter 20 cm , (2) Quartz tube 120 m in length and 3 cm in diameter, (3) one regulators to control gas rate, (5) bubbler to receive the Unwanted outputs of gases. Figure(3-5) shows a Scheme of the system CVD used in the work.



Fig.(3-5): schematic diagram of CVD system.

#### **3.6.1. Purification Process**

The process of synthesized CNTs mostly include impurities which produce from metallic and by product. The catalyst were used as catalyst for the precipitation such Fe while the ether were represent by carbonaceous materials such as carbon onions, amorphous, and graphitic carbon and unconverted carbon . Therefore, to remove these materials two steps were used for this purpose: the first was removing the products from the precipitation quartzes boats by 200 mL ethanol within an ultrasonic water bath. The second step involved immersing the black product in a 40 % H<sub>2</sub>O<sub>2</sub> solution by ultrasonic water bath. The dispersed sample was then stirred in an H<sub>2</sub>O<sub>2</sub> solution for 10 min., which left a black precipitation to dry at room Temperature for 24 h, then we obtained the black powder (MWCNT's) all this process show in Figure(3-6).

#### **3.7. Preparation of MWCNT's thin film**

In this work, we need to prepared MWCNT's thin film for applying gas sensor and solar cell, typically substrate for making gas sensor is a quartz glass plate. Before using the glass substrates, they were cut to pieces of the size of (2cm<sup>2</sup>). Then all glass substrates were cleaned in an ultrasonic bath for 10 minutes in distilled water and 5 minutes in acetone, then, dry in air, before placed inside APCVD system. The mixture of methanol and butanol as rate (50%,50%) are used for feed them into the chamber at 700°C for 30 min, finally we obtained on MWCNT's thin film .

#### 3.7.1. Experimental setup of gas sensor

The gas sensor is located inside a closed stainless steel experiment chamber and the disparity of its electrical signal is observed by an instrument. The electrical instruments have been used for sensor testing Brymen (BM850) digital multimeter for resistance measurement. The vacuum system was used to evacuate the chamber with a needle valve controller was used for mixing Resistive response the carrier and target gases at the desired concentrations and flow rates. The gas flow rates was controlled by pump the known volume of ethanol in volume chamber that already calculate. The sensors were tested in room temperature or at moderate temperatures 30°C.



Fig.(3-6): photos for the process of purification the synthesized MWCNT's (a) MWCNT deposition on quartz surface, (b) sample after clean by ethanol,(c)solution of MWCNT, (d) MWCNT with H<sub>2</sub>O<sub>2</sub>, (e) MWCNT as powder after drying, (f) MWCNT purification as powder after drying.

# 3.8. synthesized of DSSC

DSSCs was prepared as listed in Figure(3-7).



Fig.(3-7): Preparing scheme of the DSSC.

## **3.8.1.** Preparation of Glass Substrates

The typical substrate for making dye sensitized solar cell was a glass plate coated on one side with Transparent and Conductive Oxide (TCO) layer. The TCO material is thin layer of fluorine doped tin oxide (SnO<sub>2</sub>: F), also called (FTO) with conductivity (TEC-  $8\Omega$  and TEC- $15\Omega$ ) respectively. Before using the glass substrates, they were cut to pieces of ( $2cm^2 * 4cm^2$ ), then all glass substrates were cleaned in an ultrasonic bath for 5 minutes in distilled water and 5 minutes in acetone, finally, dry in air.

## 3.8.2. Preparation of MWCNTs /TiO2 Nano composite

The synthesis procedure for  $MWCNT's/TiO_2$  thin film, Include the following steps:

- 1- Solution (A): using 0.5 g of  $TiO_2$  (anatase) to dissolved in 50mL form ethanol within an ultrasonic water bath for 15min.
- 2- Solution (B) : 0.2 g of CNT's were suspended in 20mL of H<sub>2</sub>O<sub>2</sub> for 10 min. inside ultrasonic water bath. Solutions (A and B) shows in Figure(3-8).
- 3- Added B to A slowly by drop wise while utilizing ultrasonic bath for30 minutes to obtain different rate from MWCNT's (0.005, 0.01)gshows in Figure(3-9).



Fig.(3-8): Show , (a) solution of 0.5g TiO<sub>2</sub>, (b) solution of 0.2 g MWCNT  $+20ml \ H_2O_2$ 



Fig.(3-9): shows the different rate of solution for TiO<sub>2</sub>/MWCNT, (a)0.01 MWCNT,(b) 0.005 MWCNT

#### **3.8.3.** Preparation of Working Electrodes (Photo anode)

After the FTO glass was fully clean, a masking tape was placed on the glass on the side that has the FTO layer . The mask was required to ensure that an area is left so that electric contacts can be placed on the glass. Then to prepare  $TiO_2$  layer and  $TiO_2/MWCNT$  with different rates(0.005-0.01)g layer deposition by Doctor-blade method,  $TiO_2$  paste, of a very small amount was applied to the device .

Using a glass slide with the gentle sweep, the excess paste was taken off to produce a thin layer of TiO<sub>2</sub>. The glass with the TiO<sub>2</sub> layer was left to dry for 5 to 10 minutes and then the tape was removed. The FTO glass with TiO<sub>2</sub> layer was heated in the stirrer from 50°C to 250°C with gradual increments of 50°C at 10 minutes intervals the samples were observed to change colors with increasing temperatures .

Then, the substrates of  $TiO_2$  and MWCNTs /TiO<sub>2</sub> went through the process of annealing for 30 min. at 450°C temperature to remove the impurities and viscous solvent. These are then cooled down at room temperature to escape the slides cracking earlier to the immersing them in a solution of dye.

Electrodes are dipped into the dye solution of 10mg dissolved in 50ml ethanol and placed in dark place for 12 hours. Afterwards, glass is washed with ethanol and air dried for five minutes time. all process shows in Figure(3.10).



Fig.(3-10): photos for the process of prepare an anode ,(a) TiO<sub>2</sub>/MWCNT films before annealing, (b) films annealing ,(c) solution of dye, (d) films in solution of dye, (e) films after immersing in a solution of dye

## 3.8.4. Preparation of electrolyte and counter electrode

DSSC counter cathode comprised of thin Silver nitrate layer while taken catalyzed surface for regeneration of electrolyte. This was formed by operating the solution of the precursor of Silver nitrate on the FTO coated substrates and covered with a black smoke. Later, cathode and anode are united to avoid further leakage of electrolyte Silver nitrate 0.5 g. The solution is kept in a black bottle. This solution is used as an electrolyte. The electrode is set by exposing the FTO-plated glass conductor to candlelight for 2-4 minutes leaving a black soot film of carbon on the glass Figure (3.11) seen that process.



Fig.(3-11): Photos for preparation of cathode , (a) the film from silver nitrate, (b) the films after coated by black soot.

## **3.8.5. Electrolyte of DSSCs**

Iodine 0. 5g and potassium iodide 0. 5g were mixed in 10 mL of polyethylene glycol 200, the solution is kept in a black bottle. This solution is used as an electrolyte. An ionic liquid electrolyte containing iodide and tri-iodide redox couple is the medium of choice due to its non-flammability, high thermal stability, low vapor pressure, and low toxicity.

## 3.8.6. Solar cell assembly and measurements

The electrodes were composed with each other and got together face to face to keep the surface coated  $TiO_2$  paste and face carbon coated in touching was set in the contact between the two glass work and by electrolytes the electrolyte was uniformly spread throughout the  $TiO_2$ nanoparticles, as seen below Figure(3-12) :



Fig.(3-12): photos for Solar Cell assembly.

When completed, the DSSC system was activated with a light source for a (1000 xenon lamp) set up in a 500W/m<sup>2</sup> solar simulator. The lamp shines almost sunlight. The test temperature was  $23^{\circ}C-25^{\circ}C$ . The Cell performance was measured using Cell Tester MODEL (CT100AAA) as shown in Figure(3-13).



Fig.(3-13): photo for Cell Tester MODEL (CT100 AAA).

# **3.9.** Characterizations techniques

MWCNT's were characterized using X-ray diffraction (XRD),Field Emission Scanning Electron Microscopy (FE-SEM),Raman Microscopy, transmission Electron Microscopy (TEM) ,Optical Measurement.

## **3.9.1. X-Ray Characterization**

To characterize the samples of MWCNTs, it has been employed XRD system used in this study type (shimadzu 6000). This system is available in the University of Bagdad ,the measurement conditions were listed as follows .

X-ray	tube		
	target	:	Cu
	voltage	:	40.0 (kV)
	current	:	30.0 (mA)
Slits			
	Auto Slit	:	not Used
	divergence slit	:	1.00000 (deg)
	scatter slit	:	1.00000 (deg)
	receiving slit	:	0.30000 (mm)
Scann	ing		
	drive axis	:	Theta-2Theta
	scan range	:	5.0000 - 100.0000 (deg)
	scan mode	:	Continuous Scan
	scan speed	:	4.0000 (deg/min)
	sampling pitch	:	0.0200 (deg)
	preset time	:	0.30 (sec)

## **3.9.2. FE-SEM Characterizations**

MWCNT's were analyzed using FE-SEM . Using an instrument (mode Custom) FEI NOVA NanSEM450, in the University of Tehran, Iran.

## **3.9.3. TEM characterization**

Using an instrument called (JEM-2100F Japan). This system is available in Day Petronic Company in Iran Tehran.

## **3.9.4.Raman spectroscopy characterization**

Using Raman spectroscopy Senterr aInfinty Bruker 1 in laboratories of Day Petronic Company in Iran Tehran to examine the MWCNTs.

## **3.9.5.** Optical Measurements

The optical transmission and absorption spectra of the  $(TiO_2/MWCNT)$  films in the visible and NIR regions ( 300 -900 nm) have been recorded using (UV–Visible1800 Double beam spectrophotometer) made by (Shimadzu), Japanese company.



#### 4.1. Introduction

In this chapter, the following cases are introduced:

- 1-Synthesize of MWCNT's using CVD by mixing different ratios of alcohol( Methanol+ Butanol). The structure and morphology of the fabricated materials are characterized by Raman spectroscopy, FE-SEM, EDS, TEM, and XRD.
- **2** Preparation of CNT's film using CVD that was characterized by FE-SEM and applied as gas sensor.
- **3** Preparation two ratios of  $TiO_2$  /MWCNT's include MWCNT's from Aldrich and synthesized (0.01, 0.005)g respectively. The products were investigated morphology, topography, and crystal structures using FE-SEM, and EDS,

**4-** Dye sensitized solar cells (DSSCs) assembly, and I-V potentiostat properties were done. The DSSCs were fabricated using anodes which includes synthesized and commercial MWCNTs after doping with TiO<sub>2</sub>. The cathode was fabricated by coating FTO with sliver nitrite and black soot.

#### 4.2. Raman spectroscopy

Raman technique was commonly used to identify and made the final decision for tubular structure of carbon CNTs. Every band with Raman spectrum refer to a specific vibrational frequency of the molecule. The vibrational frequency and hence the position of the Raman band is highly sensitive to the orientation of the bands and weight of the atoms[128].

The Table (4-1) shows the style and contents of the samples used in this study from Figures (4-1), (4-2), (4-3), (4-4) and (4-5) shows the Raman spectrum of a CNT's in which well-defined D and G bands are

observes. the values and ratios of  $I_D/I_G$  are presented in the Table(4-2). When analyzing D and G modes and the ratios of their  $I_D/I_G$  intensity, certainly, it can be seen multi-walled carbon nanotubes, besides, disappear RBM bands in spectra was observed in the investigations performed, which also confirms the fact that multi-walled carbon nanotubes were fabricated which is in agreement with[129]. The RBM are not present because the outer tubes restrict the breathing mode[128].

The relative intensity  $I_D/I_G$  is constant for all samples approximation, indicating that the reaction does not modify the crystalline structure of the material which is in agreement with [130]. D band originates from a hybridized vibrational mode (sp<sup>3</sup> hybridized) associated with MWCNT edges which indicated the presence of some disorder to the MWCNT structure .This band typically referred to disorder or defect band which forming with G band, the decision on the quality of nanotubes [128].

In all figures, D band was the high intensity with a width of the band and the G-band shifts to lower intensities, meaning that samples containing large amounts of MWCNTs display higher D-bands than samples containing small amounts which is in agreement with [130-135]. However, some authors suggest that MWCNT's tend to appear when there is a higher degree of defect in the nanotubes [69,136, 137].

Style of sample	contented the samples
Sample 1	Synthesized by Methanol 100%
Sample 2	Synthesized by Methanol 75% + Butanol 25%
Sample 3	Synthesized by Methanol 50% + Butanol 50%
Sample 4	Synthesized by Methanol 25% + Butanol 75%
Sample5	Synthesized by Butanol 100%

 Table(4-1): Represented style and contented the samples.

Table (4-2): Raman value of peaks D, G and intensity  $I_D/I_G$  for MWCNT's.

Number of sample	The value of the peak D cm <sup>-1</sup>	The value of the peak G cm <sup>-1</sup>	Intensity of D (I <sub>D</sub> )	Intensit y of G (I <sub>G</sub> )	The I <sub>D</sub> /I <sub>G</sub> ratios
Sample 1	1338.3	1570.83	1976.47	1899.5	1.0405
Sample 2	1329.6	1572	2104.7	2055.1	1.0241
Sample 3	1343.24	1583.77	2123.54	2028.54	1.0468
Sample 4	1344.22	1581.57	1938.49	1809.56	1.0712
Sample 5	1338.84	1584.75	1724.54	1559.01	1.1061



Fig.(4-1): Raman shift for the synthesized MWCNT's from Methanol 100% .



Fig.(4-2): Raman shift for the synthesized MWCNT's from

Methanol 75% + Butanol 25% .



Fig.(4-3): Raman shift for the synthesized WCNT's from Methanol 50% + Butanol 50% .



Fig.(4-4): Raman shift for the synthesized MWCNT's from Methanol 25% + Butanol 75%



Fig.(4-5): Raman shift for the synthesized MWCNT's

from Butanol 100%.

#### 4.3. Morphological Analysis

#### 4.3.1. FE-SEM analysis for synthesized MWCNT's

The samples were characterized by using Field Emission Scanning Electron Microscopy (FE-SEM), Figures (4-6),(4-7),(4-8),(4-9),(4-10) shows images that reveal CNT's variation morphology which grown on the catalyst particles by using CVD method. The synthesized MWCNTs were variant in shapes (bent), helical, straight alignment ,branched and coils MWCNT structures, as a result of the size and density of nucleation which is in agreement with [138]. Figure (4-6) illustrates the images at 15 000 x, 30 000 x, 60 000 x and 120 000 x magnifications of MWCNT's obtained from sample1 have larger outer diameters, thick walls shorter length and most of the product consists of bend, curly and helical shaped structures.

Which means that for this specific MWCNT's synthesis method, methanol has higher trend to surround iron nanoparticles instead of the promotion of the formation of the cylinder structures required to obtain large CNTs which is in agreement with [130,138]. FESEM micrograph of sample5 at 15 000 x , 30 000 x , 60 000 x and 120 000 x magnifications are shown in Figure (4-7), the MWCNT's obtained from Butanol nanotubes. From the Figure, show the best CNTs/amorphous carbon ratio, and CNTs from butanol with different shape and size, thus this molecule seems to have the most adequate structure to promote the formation of hexagonal rings, as well as, the formation of the cylinder structures required to generate the nanotubes which is in agreement with [130,138].



Fig.(4-6): FE-SEM images of Samplel (a) 15 000x (b) 30 000x (c) 60 000x (d) 120 000x magnifications.



Fig.(4-7): FE-SEM images of Sample5 (a) 15 000x (b) 30 000x (c) 60 000x (d) 120 000x magnifications.

Moreover, in Figure(4-8), (4-9) illustrates the images at  $15\ 000\ x$ ,  $30\ 000\ x$ ,  $60\ 000\ x$  and  $120\ 000\ x$  magnification of the samples 2 and 3. From Figures, show MWCNT's growth that are oriented perpendicular to the substrate homogenous in lengths and straight aligned lattice MWCNT's growth of quartz substrates under the same growth conditions which is in agreement with [139].

A hypothesis is proposed in which the precipitated carbon shell on the outer surface of the metal catalysts guides the alignment along the crystal lattice but not the catalysts themselves which show the emergence of straight aligned to MWCNT growth, meaning that CNTs are oriented perpendicular to the substrate. They all are straight aligned [140].

FESEM micrographs at 15 000 x , 30 000 x , 60 000 x and 120 000 x magnifications of sample 4 are shown in Figure (4-10). From the Figure, a variety of shapes, sizes and wall thicknesses are observed.



Fig.(4-8): FE-SEM images of Sample2 (a) 15 000x (b) 30 000x (c) 60 000x (d) 120 000x magnifications.

#### **Chapter Four**



Fig.(4-9): FE-SEM images of Sample3 (a) 15 000x (b) 30 000x (c) 60 000x (d) 120 000x magnifications.



Fig.(4-10): FE-SEM images of Sample4 (a) 15 000x (b) 30 000x (c) 60 000x (d) 120 000x magnifications.

From Table(4-2) which listed the value of diameters, lengths and average weight of the product, which could be seen that sample 3 was higher product as compare with anther samples . Average values of these parameters were obtained by measuring the length and diameter of the most representative nanotubes from each sample which is in agreement with [130].

In all Figures (4-6), (4-7), (4-8), (4-9) and (4-10) many bending were observed for all synthesized product ,that can be related to the sheets bend when their height is over a certain level. The nanotubes within each sheet confine the nearest neighbors and attract the outermost nanotubes to their neighbors Van der Waals force, thereby producing oriented growth which is in agreement with [3].

Finally, we must know that the difference in shapes of MWCNT's are highly desired for device application such as transistors, sensors, light emitters, logic circuits, and other system [141-144]. The most attractive approach is direct growth by CVD with an external force [145].

It should be noted that the Image-J program was used to calculate the diameters and lengths of all samples used in this study

samples	Diameters (nm)	Lengths (nm)	Weight (g)
Sample 1	40-200	2000 - 2350	0.4
Sample 2	30 - 150	2359 - 3074	0.3
Sample 3	30 - 140	2000-2700	0.9
Sample 4	25-200	1000-2600	0.3
Sample 5	20-100	1000-4200	0.3

# Table (4-3): The lengths and diameters of synthesized MWCNT's andweight of samples after preparation.

## 4.3.2. TEM analysis for synthesized MWCNT's

The TEM images are demonstrated in Figure (4-11). It proved the formation of multi-wall carbon nanotubes, and the appearance of different shapes such as straight, bent and vertical alignment as well as the appearance of Y- junction as in Figure (4-11-c). The presence of iron particles mainly, suggesting that a tip-growth mechanism might be predominant as in Figures (4-11-a). The average outer diameter  $\approx 28-55$  nm, inner diameter range  $\approx 2.8-5$  nanometers , average number of turns  $\approx$  11-21Wall and length ratio  $\approx 1.5-2.5 \ \mu m$  [146]. The Image-J program was used to calculate the results .



Fig.(4-11): TEM photographs of synthesized MWCNT's using CVD, a. helical and straight shape, b. curve shape with open end, c. Y-junction shape and d. curly shape

#### **4.3.3.Energy dispersive X-ray spectroscopy (EDS)**

The EDS analysis was depend to applying qualitative and quantitative measurements of chemical composition of the tested sample in micro-areas, the quantitative EDS results are listed in table (4-4). Figures (4-12), (4-13), (4-14), (4-15) and (4-16) shows an EDS spectrum of MWCNTs synthesized by the CVD technique from different ratio of C1/C4 at 700°C on the quartz as support impregnated with Ferrocene, which was used to grow MWCNTs. The spectrum shows four strong peaks, for Carbon, Oxygen and two for Fe. The C refers to carbon materials, mostly refer to CNTs growth on Fe that covers the surface of the quartz boat. The O refers to the groups of oxide which are produced by a purification process by using  $H_2O_2$ . The two peaks for Fe indicates that the growth of CNTs originated from Fe or Fe carbide particles on the quartz substrate[8]. As for the elements( P, Al, Si, N, Ti) which were clearly apparent in the analysis, they are often due to impurities from different sources.

Number of	С	Fe	$\mathbf{O}_2$	
sample	concentration	concentration	concentration	
Sample 1	87.58	5.37	6.56	
Sample 2	87.17	6.11	4.56	
Sample 3	84.62	5.08	8.15	
Sample 4	79.74	5.01	14.69	
Sample 5	82.58	11.52	5.83	

 Table (4-4): The quantitative EDS results for all samples.



Fig.(4-12) : EDS analysis of sample1 by CVD at 700°C.



Fig.(4-13) : EDS analysis of sample2 by CVD at 700°C.


Fig.(4-14) : EDS analysis of sample3 by CVD at 700°C.



Fig.(4-15) : EDS analysis of sample4 by CVD at 700°C.



Fig.(4-16) : EDS analysis of sample5 by CVD at 700°C.

#### **4.4. Structural Properties of CNT**

## 4.4.1. XRD Analysis of MWCNT's

The XRD patterns of MWCNT's are displayed in Figure (4-17), it can be noticed that all the samples exhibit diffraction peaks around  $(2\theta \approx 62.1^{\circ}, 35.5^{\circ}, 43.7^{\circ}, 54^{\circ}, 57^{\circ})$  and  $26.09^{\circ}$ ) referred to (002), (222), (100), (004), (104) and (015) favorite directions respectively as shown in Table (4.5), which is in agreement with (IDDC) card number 411487. For all samples as shown in Figure (4-18), the peaks around  $2\theta \approx 26^{\circ}$  and  $43^{\circ}$ which belongs to (002) and (100) respectively in purifying MWCNT's by H<sub>2</sub>O<sub>2</sub>, and corresponds to carbon nanotubes oriented along the c-axis in accordance with previous reports available in the literature [147-151]. The peak at  $2\theta \sim 26^{\circ}$  which was strong and broad corresponded to (002) reflections of MWCNTs. A strong peak (002) in the XRD pattern shows a lower alignment of carbon nanotubes as the intensity of the (002) peak decreases monotonically with better alignment of carbon nanotubes which is in agreement with[86]. The peak at 43° for (100) plane indicated the low quality of carbon nano materials which is in agreement with [152].

The peaks near  $(2\theta \sim 35.5^\circ, 54^\circ, 57^\circ \text{and } 62^\circ)$  are attributed to the (222), (004), (104) and (015) respectively, of the Fe substrate which was used as a catalyst for the precipitation methods. The positions of the peaks and the presence of more than one diffraction peak lead to the conclusion that the samples are polycrystalline in nature with a hexagonal crystalline structure.

It can be noticed also that the lattice constants (a=b, c) for MWCNT's are equal to 2.3Å and 3.8Å respectively as shown in Table (4-6) which indicates that the synthesized samples have the nearest (a=b, c) values to the standard lattice constants 2.47Å and 3.724Å respectively as shown in Table (4-6).

The width of the diffraction peaks is an indication of the nano-size of the prepared material, the interlunar spacing was calculated to be d(002)=3.413 Å for all samples as shown in Table (4-5).

The length and width of the peaks were commonly used to recognize the nature of crystal size. the width increases with reducing intensity or length, which refers to exist CNT in amorphous crystal form. typically, the impurities influence Directly on the position of peaks due to low intensity of the peaks compared with the impurities[8].



Fig.(4-17): X-ray diffraction pattern of synthesized MWCNT's.

Number of	20	d <sub>hkl</sub>	hkl	FWHM
sample	(deg)	Exp.(Å)		(rad)
Sample 1	26.09	3.41306	002	0.021746
	35.55	2.5207	222	0.010757
	43.75	2.0675	100	0.015351
	54.19	1.7039	004	0.013257
	57.39	1.6044	104	0.009943
	62.17	1.4920	015	0.011164
Sample 2	26.09	3.41306	002	0.023171
	35.59	2.5207	222	0.009791
	43.33	2.0675	100	0.0157
	53.75	1.7039	004	0.013606
	57.39	1.6044	104	0.010117
	62.17	1.4920	015	0.011222
Sample 3	26.03	3.4130	002	0.025526
	35.49	2.5207	222	0.011745
	43.10	2.0675	100	0.023375
	53.74	1.7039	004	0.009768
	57.39	1.6044	104	0.00942
	62.17	1.4920	015	0.011164
Sample 4	26.05	3.4130	002	0.024108
	35.51	2.5207	222	0.011047
	43.08	2.0675	100	0.02198
	53.75	1.7039	004	0.00314
	57.39	1.6044	104	0.010466
	62.17	1.4920	015	0.012211
Sample 5	26.17	3.4130	002	0.020497
	35.83	2.520	222	0.010839
	43.16	2.0675	100	0.019188
	53.74	1.7039	004	0.014653
	57.39	1.6044	104	0.009768
	62.17	1.4920	015	0.010815

# Table (4-5): The value of $(2\theta)$ for peaks of synthesized MWCNT's.

## 4.4.2 The crystallite size (D<sub>av</sub>)

#### I. Calculation of crystallite size using Scherer's formula:

The crystallite size of MWCNT's for all samples, can be calculated by using Scherer's formula (2.6). It is observed that the crystallite size for the sampl1, sample2, sample3, sample4 and sample5 equals (11.9,12,11.8,17.2 and 11.6) nm respectively, and it increases for the sample4, as shown in Table (4.2). The larger crystallite size values indicate better crystallization of the samples [152,153,]. The average particle size of the treated purified MWCNTs nanoparticles by  $H_2O_2$  was estimated by using the standard Scherrer formula [154,155], there were six peaks as was shown in table (4-6).

#### **II.** Calculation of crystallite size by Williamson-Hall analysis:

The crystallite size can be estimated using W-H equation (2.7). A plot is drawn with  $(4\sin\theta)$  along the x-axis and  $(\beta \cos\theta)$  along the y-axis for all samples as shown in Figure (4.9).From the linear fit of the data, the crystallite size was estimated from the y-intercept, and the microstrain S, from the slope of the fit. The microstrains are induced during the formation nanomaterial, and will be raised from stretching or compression in the lattice. The microstrain is caused by varying displacements of the atoms with respect to their reference lattice positions [156]. From the results, it was observed that the microstrain value decreases while the crystallite size increases and this is in agreement with Bari et al. [156]. Figure (4-18) shows the W-H plots for all samples and Table (4.6) summarizes the results obtained from W-H analysis. The values of microstrain are negative for all the samples which indicate the occurrence of compression in the lattice .

## **4.4.3 Dislocation Density (δ)**

The dislocation density is the measure of amount of defects in a crystal. The small value of dislocation density obtained in the present work confirmed good crystallinity of sample 4. According to equation (2.10), there is inverse relation between dislocation density and crystallite size so that dislocation density decreases when the values of crystallite size increases, as shown in Table (4-6).

Table (4-6): Structural parameters for all samples and comparison betweenScherrer and W.H methods of MWCNT's.

Sample		Sample1	Sample2	Sample3	Sample4	Sample5	
D <sub>av</sub> (nm)	Scherrer	11.9	12	11.8	17.2	11.6	
	W-H	5.67	5.67	4.28	4.6	4.69	
δ (line. cm <sup>-2</sup> )*10	-3 Scherrer	7.06	6.9	7.1	3.3	7.43	
	W-H	31.1	31.1	54.58	47.25	45.4	
Micostrain (S) *10 <sup>-3</sup>		-7.73	-13.83	-12.05	-11.27	-29.53	
Lattice	2.47						
(a=b) Å		2.3					
Lattice	IDDC	6.724					
constant ( c ) Å	Calculated			6.8			



Fig.(4-18): The W.H analysis of synthesized MWCNT's.

# 4.5 Gas Sensing Result

### 4.5.1.Sensing Characteristics at Room Temperature

The response (S=R  $_{air}/R_{gas}$ ) of the sensors was explored for ethanol gas for different mixing ratios. In general, the resistive gas sensor based on MWCNTs demonstrated great potential for detecting ethanol at room temperatures. The advantages of the design include simple structure, very low nanotube loading, easy to measure, demonstrated functionality in air, and low humidity dependency. On the other hand, the issue with the sensor recovery needs to be continuously addressed to improve the long term sensor performance. The undesired resistance drift must be minimized the sensor function properly during the multiple-cycled gas detection applications. FE-SEM micrographs at 150 000 x, 30 000 x, 50 000 x and 120 000 x magnifications of MWCNT's film is shown in Figure (4-19). The FE- SEM image of MWCNTs film is shown to obtained on quartz substrate after the catalytic decomposition of ferrocene using the CVD method at a high temperature of 700°C using (Methanol 50% + Butanol 50%) as a source of carbon. From Figure (4-19) dense forests of MWCNTs are visible in FE-SEM micrographs. So, uniform and meadow-like grown MWCNTs . It seems to be linked to the effect of starting catalyst particles size on nanotube diameter [157,29]. As we used a relatively high flow rate of  $N_2$  (200 ml/min), some iron nanoparticles were driven away from the furnace, decreasing the number of catalyst particles inside the furnace, resulting in low collisions between the particles, which leads to the formation of smaller clusters and formation of MWCNTs with rather narrow diameter. From Figure(4-19,d) shows the range of diameters about (41-71) nm.



Fig.(4-19):FE-SEM image of MWCNT's film at (a) 150 000x (b) 30 000x (c ) 50 000x (d ) 120 000x magnifications

#### 4-5-2 Gas Sensing Characterization

After the sensors were purged with argon gas, they were used to detect ethanol gases. Figure(4-20) shows the electrical resistance variations of MWCNTs film sensor to ethanol gas. It demonstrated that our sensor is highly sensitive with a fast response time of 30 seconds. It also indicates that the recovery of the sensors is relatively fast and complete. This can stem from the fact that ethane is a saturated hydrocarbon which leads to the weak interaction between tested gas and CNTs molecules. We observed

that the resistance of CNTs increased for ethanol exposures. This increase can be described as follows: Since it is known that ethanol is an electron donor gas [158]. When the sensors are exposed to this gas, it donates electrons to the valence band of CNTs, thereby increasing the separation between the Fermi level and the valence band, resulting in hole depletion in the p-type semiconductor CNTs and increasing the electrical resistance[159].



Fig.(4-20): The varation of resistance with time for MWCNT film synthesized at 700°C, ethanol gas sensing , (a) 250ppm, (b) 500ppm,(c)750 ppm.

Figure (4-21) shows the variation of sensitivity as a function of the time, a maximum sensitivity of 3.9 was recorded by the MWCNT sensor at 750 ppm from ethanol gas. Table(4-7) shows the response times recovery times and sensitivity for all gas mixing ratio.



Fig.(4-21): The variation of sensitivity with time for MWCNT film, ethanol gas sensing, (a) 250ppm,(b) 500ppm,(c) 750ppm.

Gas volume	Response time (s)	Recovery (s)	Sensitivity %
250 ppm	120	69	0.75
500 ppm	180	150	2.6
750 ppm	154	70	3.9

Table (4-7): Response time ,recovery time and Sensitivity% of MWCNT film.

As its apparent from Figure (4-22), the response of MWCNT film sensor sensitivity to methanol gas of different mixing ratio. It is obvious the sensor sensitivity to ethanol gas increases gradually with raising of ethanol ratio.



Fig.(4-22): Plot of Sensitivity vs. gas ratio for MWCNT film.

Figure (4-23)exhibits both response and recovery times toward the ethanol concentrations. Figure (3.64) exhibits an increase in the response times in comparison with recovery times. The highest response was about 179 s at 500 ppm ethanol ratio and the shortest response and recovery times are about 124.2 s and 67.6 s respectively at the same above ethanol concentration (250 ppm).



Fig.(4-23): Plot of response time and Recover time vs. gas ratio of MWCNT sensor.

# 4.6. Dye Sensitized Solar Cell Result

## **4.6.1.** FE-SEM morphological structure

Figures (4-24), (4-25), (4-26), (4-27) and (4-28) illustrates the images at 240 000 x, 240 000 x, 120 000 x, 240 000 x, 30 000 x, 120 000 x, 30 000 x, and 60 000 x magnifications respectively, of TiO<sub>2</sub> with different MWCNT concentration and type as represented in Table (4-8). All these images explained the well-formed MWCNT inside TiO<sub>2</sub>, prepared by MWCNT/TiO<sub>2</sub> as powder clearly indicates that the image morphology strongly changes with the increase of CNT amount. For low concentration of CNT , the image appears as a bulk of TiO<sub>2</sub> anatase grains with randomly insertion of carbon nanotubes, the tubes fill the interstices between grains by covering the grains or changing the structure. In this case, we can associate the mixing to doping process of TiO<sub>2</sub> anatase bulk.

For images ( 2,3,5 ) the structure changes while FS-SEM images appear as a bulk of TiO<sub>2</sub> anatase grains with insertions of large clusters of CNT. Finally, for image 4, the formation of a grainy structure composed of cluster of CNT and TiO<sub>2</sub> anatase. Its surface is homogeneous [160], solar cell and there are no cracks found on the surface area. This condition will help increase the mechanism of dye absorption due to the high porosity level in the MWCNT/TiO<sub>2</sub> films. The dye molecules that occupy within cracks will have no bonding with TiO<sub>2</sub> nanoparticles therefore would be vanished in the electrolyte solution. This will decrease the photovoltaic performance since the cell does not have enough dye molecules to transmit the electron in the metal oxide [161].

Number of image	Type of powder	ratio	
Image 1	TiO <sub>2</sub>	100%	Pure
Image 2	MWCNT/TiO <sub>2</sub>	0.005 MWCNT	Aldrich
image 3	MWCNT/TiO <sub>2</sub>	0.01 MWCNT	
Image 4	MWCNT /TiO <sub>2</sub>	0.005 MWCNT	synthesized
Image 5	MWCNT/TiO <sub>2</sub>	0.01 MWCNT	

### Table (4-8): Represented TiO<sub>2</sub> with different MWCNT's concentration and type.



Fig.(4-24):Shows the FE-SEM surface morphological structure of imagel (a)240 000x (b)240 000x magnifications.



Fig.(4-25):Shows the FE-SEM surface morphological structure of image2 (a)240 000x (b)240 000x magnifications.



Fig.(4-26):Shows the FE-SEM surface morphological structure of image3 (a)120 000x (b)240 000x magnifications.



Fig.(4-27):Shows the FE-SEM surface morphological structure of image4 (a)30 000x (b)120 000x magnifications.



Fig.(4-28):Shows the FE-SEM surface morphological structure of image5 (a)30 000x (b)60 000x magnifications.

## 4.6.2. Energy dispersive X-ray spectroscopy (EDS)

Figures (4-29), (4-30), (4-31), (4-32) and (4-33) represent the EDS analysis of the elemental composition were performed by EDS spectroscopy. The images contain several elements such as titanium, carbon and oxygen without any impurity or unknown elements. As for the elements, which were clearly apparent in the examination, they are often due to pollutants obtained from the examination of other samples in the same apparatus. The intensity of most the peaks were witnessed small change due to additions materials with  $TiO_2$ .



Fig.(4-29):EDS analysis of image1 using CVD.



Fig.(4-30):EDS analysis of image2 using CVD.



Fig.(4-31):EDS analysis of image3 using CVD.



Fig.(4-32):EDS analysis of image4 using CVD.



Fig.(4-33):EDS analysis of image5 using CVD.

#### **4.6.3. Optical Properties**

The optical measurement results include relations of the absorbance with wavelength for  $TiO_2$  /MWCNT's films, and computing some optical parameters like absorption coefficient, extinction coefficient, real and imaginary part of dielectric constant, and optical energy gap.

#### a. UV-VIS Spectroscopy of Dyes (Absorption spectrum of Z907)

The absorption spectrum of Z907 dye in ethanol solvent is shown in Figure (4-34). There are two absorption peaks at (316 and 527 nm), therefore these bands cover a part of the visible region. The Ruthenium Z907 dye absorption spectrum extends only to 700 nm; therefore, it has nearly no absorption band in the infrared region and causes limit solar cell efficiency. The thiocyanate ion ligand is the most sensitive part of the dye (Z907), when adsorbed onto TiO<sub>2</sub> in DSSC [162].



Fig.(4-34): The absorption spectrum of Ruthenium Z907dye.

## b. Absorption spectrum of TiO<sub>2</sub>, TiO<sub>2</sub>/MWCNT films

The optical properties of the TiO<sub>2</sub> and TiO<sub>2</sub> with different ratios of the MWCNTs films can be seen in Table (4-8). The as-deposited thickness was 10 $\mu$ m which annealed at 450°C for 30 minutes and determined by using UV-VIS spectroscopy within region of (200-1100 nm) before and after annealing as shown in Figures (4-35) and (4-36). A fundamental absorption edge in the UV region of all films were behaved shift towards a higher wavelength, refers to narrow band gap caused by MWCNTs represented in Figure(4-35). A typical absorption with an intense transition in the UV region was observed in the spectra of all films, assignable to the intrinsic band-gap absorption of TiO<sub>2</sub> for electron transition from the valence band to the conduction band [163,164].

In the UV region, the absorption is very high compare with visible region which may related to  $TiO_2$  can be used as UV blocker while organic solar cells avoid degradation by UV rays [165]. The strongest absorption in the UV region was observed for Film 4. Increasing the amount of MWCNTs in the nanocomposites resulted in a decrease the absorption. Increase visible light absorption can be explained by CNT doping which forms inter band gap states with  $TiO_2$ , resulting in reduced band gap and consequently shifting the absorption edge to the visible region[166].

After annealing results are shown in Figure (4-36), the absorption edge is shifted to a shorter wavelengths (high energy) which agree with the result of Vorontsov when reported shift absorption to a shorter wavelength due to the quantum-size effect [167]. It is possible to observe increase the intensity of absorption spectrum, which refer to specific wavelengths for the absorption capacity.

Number of Film	Type of powder	ratio	
<b>T</b> '1 1	<b>TT</b> 'O	1000/	D
Film I	$I_1O_2$	100%	Pure
Film 2	MWCNT/TiO <sub>2</sub>	0.005 MWCNT	
Film 3	MWCNT/TiO <sub>2</sub>	0.01 MWCNT	Aldrich
Film 4	MWCNT /TiO <sub>2</sub>	0.005 MWCNT	
Film 5	MWCNT/TiO <sub>2</sub>	0.01 MWCNT	Synthesized
			-

Table (4-9): 7	<b>FiO<sub>2</sub> and TiO</b> 2	with different ratios	s of the MWCNT's films.
----------------	----------------------------------	-----------------------	-------------------------



Fig.(4-35): Absorbance vs. wavelength of  $TiO_2$  /MWCNT films ,

before annealing.



Fig.(4-36): Absorbance vs. wavelength of  $TiO_2$  /MWCNT films , after annealing.

#### c. Absorption Coefficient (α)

The absorption coefficient was calculated using equation (2-15). It have been noticed that all the prepared films have low absorption coefficient in visible range of the spectrum, and this could be seen in Figures (4-37) and (4-38) which shows the relation between the absorption coefficient ( $\alpha$ ) with photon energy (h $\upsilon$ ) of TiO<sub>2</sub>/MWCNT films before and after annealing. The absorption coefficient increases with increase in photon energy (h $\upsilon$ ). The absorption coefficient value depends on absorbance. TiO<sub>2</sub>/MWCNT films has a value of absorption coefficient ( $\alpha$   $<10^4$  cm<sup>-1</sup>) which causes the increase of the probability of the occurrence of indirect transitions. The absorption coefficient increases in film4 before and after annealing as shown in Figure (4-37) and (4-38).



Fig.(4-37): The Relation between absorption coefficient and photon energy of  $TiO_2$  /MWCNT films before annealing.



Fig.(4-38): The Relation between absorption coefficient and photon energy of TiO<sub>2</sub> /MWCNT films after annealing.

# 4.6.4. Optical Energy gap (Eg)

The energy gap values depend in general on the crystal structure of samples, the arrangement and distribution of atoms in the crystal lattice, also affected by crystal regularity. The optical energy gap ( $E_g$ ) was derived assuming allowed direct transitions between the edge of the valence and conduction band. The energy gap was calculated according to Tauc's plot graph between ( $\alpha hv$ )<sup>2</sup> and (hv) in eV an obtained a straight line gives the value of the direct energy gap. The extrapolation of the straight line to

 $(\alpha hv)^2 = 0$  gives values of the direct band gap of the material before and after annealing ,this could be seen in Figures (4-39) and (4-40) respectively.

It can be noticed that the band gap values increases after annealing temperature which is in agreement with [168]. The reason for this is due to the presence of carbon, which enhances the absorption of titanium, as it helps to achieve electronic transmission faster because it has higher conductivity and at the same time it works as an electron gain and is a so-called blocker of the return of electrons when stimulated in  $TiO_2$  and this has caused the absorption of the absorption to a longer wavelength, less energy[163,134]. However, many reports stated that the change in the optical band gap energy with composites may be attributed to the changes in homogeneity and crystallinity of the film, caused by differences in experimental conditions, mainly the homogeneity of suspension and the rapid cooling to room temperature [168].

The decease of crystallite size causing increase in the band gap energy which gradually shift of the absorption edge towards a shorter wavelength. This resulted in the change in energy band structure, with separation of individual energy levels and the increase in effective optical band gap of the semiconductor as compared with bulk [169]. Table (4-10) shows the indirect band gap values for this work .



Fig.(4-39): The energy gap for TiO<sub>2</sub>/MWCNT films

before annealing temperature.



Fig.(4-40): The energy gap for TiO<sub>2</sub>/MWCNT films after annealing temperature.

Samples		Film 1	Film2	Film3	Film4	Film5
E <sub>g</sub> (eV)	Before annealing	2.00	2.25	2.19	2.035	2.05
5	After annealing	3.24	3.23	3.22	3.29	3.25

Table (4-10): The energy gap for TiO<sub>2</sub> /MWCNT films.

The energy gap can be estimated according to Tauc's plot graph between  $(\alpha hv)^{1/2}$  and (hv) in eV an obtained a straight line gives the value of the indirect energy gap. The extrapolation of the straight line to  $(\alpha hv)^{1/2}$ = 0 gives values of the indirect band gap of the material before and after annealing ,this could be seen in Figures (4-41) and (4-42) respectively. Table (4-11) shows the indirect band gap values for this work .

Table (4-11): The energy gap for TiO<sub>2</sub> /MWCNT films.

Samples		Film 1	Film2	Film3	Film4	Film5
E <sub>g</sub> (eV)	Before annealing	2	2.02	2.03	1.7	1.96
8	After annealing	2.63	2.55	2.8	2.82	2.64



Fig.(4-41): The energy gap for TiO<sub>2</sub>/MWCNT films before annealing temperature.



Fig.(4-42): The energy gap for TiO<sub>2</sub>/MWCNT films after

## annealing temperature.

#### **4.6.5. Extinction Coefficient** (K<sub>o</sub>)

The extinction coefficient ( $K_o$ ) was calculated using relation (2-16). The study of extinction coefficient ( $K_o$ ) was in the range of (300 - 500)nm. Figures (4-43) and (4-44)shows the extinction coefficient as a function of wavelength for TiO<sub>2</sub>/MWCNT films before and after annealing. The extinction coefficient ( $K_o$ ) decreases at short wavelengths (300-350)nm and after that the value of ( $K_o$ ) remains constant after annealing as shown in Figure(4-44). The rise and fall in the value of ( $K_o$ ) is directly related to the absorption of light. The lower value of ( $K_o$ ) in the wavelength range (350–500) nm implies that these films absorb light in this region very easily[161]. The change in extinction coefficient with different concentration of MWCNT was not systymatic. Results show that the extinction coefficient values of prepared films are in the range of (0.001 -0.0.04) and (0.0025-0.0068) before and after annealing respectively.



Fig.(4-43): The relation between the extinction coefficient and wavelength for TiO<sub>2</sub>/MWCNT films at different concentrations before annealing.



Fig.(4-44): The relation between the extinction coefficient and wavelength for TiO<sub>2</sub>/MWCNT films at different concentrations after annealing.

#### **4.6.6. Dielectric Constant (ε)**

Complex dielectric constant ( $\epsilon$ ) consists of real dielectric constant ( $\epsilon_1$ ) and imaginary dielectric constant ( $\epsilon_2$ ) where real part ( $\epsilon_1$ ) is the normal dielectric constant and imaginary part ( $\epsilon_2$ ) represents the absorption associated with free carriers. The values of ( $\epsilon_1$ ) and ( $\epsilon_2$ ) are calculated using relations (2-18) and (2-19) respectively.

The relation between real and imaginary parts of dielectric constant and photon energy for  $TiO_2/MWCNT$  films before and after annealing are show in Figures (4-45) ,(4-46),(4-47) and (4-48). It can be seen that the real parts of dielectric constant increases as photon energy increases for film2 and film5 (3-4) eV as shown in Figure(4-45) and another films decreases . from Figure(4-46) can be seen that the real parts of dielectric constant increases as photon energy increases for all films (3-3.9) eV, and after that the value of the real parts constant. The imaginary parts of the dielectric constant increases as photon energy decreases for all films before and after annealing as shows in Figures (4-47) and (4-48). The change in real and imaginary parts of the dielectric constant with the  $TiO_2/MWCNT$  was not systematic.



Fig.(4-45): The relation between the real part of dielectric constant ( $\epsilon_1$ ) and photon energy for TiO<sub>2</sub>/MWCNT films at different concentrations before annealing.



Fig.(4-46): The relation between the real part of dielectric constant ( $\epsilon_1$ ) and photon energy for TiO<sub>2</sub>/MWCNT films at different concentrations after annealing



Fig.(4-47): The relation between the imaginary part of dielectric constant ( $\epsilon_2$ ) and photon energy for TiO<sub>2</sub>/MWCNT films at different concentrations before annealing,


Fig.(4-48): The relation between the imaginary part of dielectric constant ( $\epsilon_2$ ) and photon energy for TiO<sub>2</sub>/MWCNT films at different concentrations after annealing,

## 4.7. Current-Voltage characterization

Current-voltage (I-V) curves represent the most important and direct characterization method for DSSCs. The data include short-circuit current ( $I_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF), and energy conversion efficiency( $\eta$ ) of DSSCs[161]. The five types of TiO<sub>2</sub>, TiO<sub>2</sub>/MWCNT nanostructures, produced anode were used to assemble five DSSC's, as-described in experimental CH.(3) and Table (4-12), then subjected to I-V characterization .

The conversion efficiency was estimated by using two electrodes potential static measurements, I-V characterization in Figures (4-49), (4-50), (4-51), (4-52) and (4-53) Note that from the figures all samples have followed the behavior of a cell. The values were calculated for all cells and tabulated in table (4-13).

The DSSCs efficiencies follow the order:

# **DSSC 4 > DSSC 1 > DSSC 3 > DSSC 5 > DSSC 2**

Which means that anodized DSSC4, DSSC1 were the best semiconductors used to make the dye sensitive solar cell with the remain of other parameters constant for this work. The DSSC2, DSSC5 and DSSC3 the lowliest because the defects in the solar cell manufacturing leads to the decrease of the shunt resistance, and increases the series resistance. The excessive CNT/TiO<sub>2</sub> content might cause aggregation of MWCNTs, which undermines the separation of TiO<sub>2</sub> particles, thus leading to larger cracks formed. Moreover, with increase in quantity of TiO<sub>2</sub>/CNT powder, the number of cracks on the surface of the films increased accordingly, and the increase in number of these cracks might decrease dye adsorption. The dye molecules staying in cracks and having no bonding with TiO2 would be lost in the electrolyte solution. Hence, there were not sufficient dye molecules to transmit electrons to the semi-conductive oxide, resulting in reduced conversion efficiency of DSSCs[161].

Table (4-12): TiO<sub>2</sub>,TiO<sub>2</sub> /MWCNT nanostructures produced anode were used to assemble five DSSC's.

Number of cell	Type of anodized	
DSSC 1	TiO <sub>2</sub>	Pure
DSSC 2	0.005 MWCNT/TiO <sub>2</sub>	Aldrich
DSSC 3	0.01 MWCNT/TiO <sub>2</sub>	
DSSC 4	0.005 MWCNT/TiO <sub>2</sub>	synthesized
DSSC 5	0.01 MWCNT/TiO <sub>2</sub>	

 Table (4-13): The photovoltaic parameters of DSSC's.

Number	V <sub>oc</sub>	I <sub>sc</sub>	<b>R</b> <sub>sh</sub>	Vm	I <sub>m</sub>	P <sub>m</sub>	FF	Eff%
of cell	(mV)	(µA)	( kΩ)	(mV)	(µA)	(µW)		
DSSC 1	593	440.81	10.6k	304	235.74	71.66	0.274	0.72%
DSSC 2	79.7	26.09	979Ω	50.1	15.79	790.29	0.380	0.01%
DSSC 3	400.3	34.91	2.84k	210.1	17.08	3.69	0.257	0.36%
DSSC 4	595.6	340.56	<b>84.8</b> k	395.4	209.56	82.86	0.409	0.83%
DSSC 5	466.3	81.45	10.17k	230.2	41.47	9.55	0.251	0.1%

### **Chapter Four**



Fig.(4-49): Light I-V Measurement (Test report) for DSSC 1.



Fig.(4-50 ): Light I-V Measurement (Test report ) for DSSC 2.

### **Chapter Four**

I[A]



Fig.(4-51): Light I-V Measurement (Test report) for DSSC 3.



Fig.(4-52): Light I-V Measurement (Test report) for DSSC 4.



Fig.(4-53): Light I-V Measurement (Test report) for DSSC 5.

## **4.8.**Conclusions

**Chapter Four** 

The following conclusions can be drown from the present work:

- 1. The growth of MWCNTs, using CVD of technique, were different shapes.
- 2. The growth of MWCNTs, from samples which synthesized (Methanol  $_{50\%}$  + Butanol  $_{50\%}$  and Methanol $_{75\%}$  + Butanol $_{25\%}$ ) were vertically aligned.
- 3. The highest amount of MWCNT was obtained from the sample (Methanol  $_{50\%}$  + Butanol  $_{50\%}$ ).
- 4. The sensitivity of MWCNTs sensor deposited on quartz prepared by CVD increases with increases the gas flow ratio.

- 5. The success of the process of loading MWCNT for two type commercial and synthesized on TiO<sub>2</sub>.
- 6. Increased energy gap for  $TiO_2/MWCNT$  films after the annealing process.
- 7. The best efficiency of DSSC of the sample  $(0.005 \text{MWCNT}_{\text{syntheized}} / \text{TiO}_2)$  was obtained ,which was 0.83.
- 8. CVD method easy and reliable to fabricate CNTs.

# 4.9. Future work

- 1. Studying the synthesis CNT using different tempura .
- 2. Studying the annealing effect at range (800-1000) °C on the MWCNTs.
- 3. Preparing a catalyst particles in different methods and study the morphology of surface to growth CNTs.
- 4. Improvement performance gas sensing, it is possible to sputter the noble metal on the surface of MWCNTs.



### <u>References</u>

- [1] Md S. R., "The Systematic Synthesis of Carbon Nanotubes from Aliphatic-Aromatic Compound Mixture Resolves Growth Uniformity and Production Complexity", Journal of Nanotechnology Research, Vol. 2, No. 1, pp. 1-9, 2020.
- [2] Zhao K., Peng R. and Li D., "Separation of nanoparticles by a nanoorifice based DC-dielectrophoresis method in a pressure-driven flow", Nanoscale, Vol. 8, No. 45, pp. 18945-18955, 2016.
- [3] Wang X., Jiang Q., Xu W., Cai W., Inoue Y. and Zhu Y., "Effect of carbon nanotube length on thermal electrical and mechanical properties of CNT/bismaleimide composites", Carbon, No.53, pp.145-152, 2013.
- [4] Hussein F. H., Abdulrazzak F. H. and Alkaim A. F., "Synthesis Characterization and General Properties of Carbon Nanotubes".
   Nanomaterials: Biomedical Environmental, and Engineering Applications, CH.1, pp.3-60, 2018.
- [5] Amiri S. S., Mirza M. and Mirza B. A., "theoretical study of Novel zigzag silicon Carbon Nanotubes", Science and Research Pioneers Institute 4th International Conference on Nanotechnology and Basic Science (ICN2016), Dubai. Emirates, 2016.
- [6] Kroto H., Heath J., Brin S., Curl R. and Smally R.,"C60: Buckminster fullerene", Nature, Vol.318, pp.162-163, 1985.
- [7] Iijima S., "Helical Microtubules of Graphitic Carbon", Nature, Vol. 354, pp.56-58, 1991.
- [8] Abdulrazzak F. H., Alkiam A. F. and Hussein F. H., "Behavior of X-Ray Analysis of Carbon Nanotubes". In Perspective of Carbon Nanotubes, Intech Open, 2019

- [9] Cheng C., Jiang X., Wang J., Chen C. and Liu R. S., "Nano-bio effects: interaction of nanomaterials with cells", Nanoscale, Vol. 5, No.9, pp. 3547-3569, 2013.
- [10] Ibrahim K. S., "Carbon nanotubes-properties and applications: a review", Carbon letters, Vol. 14, No.3, pp. 131-144, 2013.
- [11] Dichiara A., "In situ diagnostics for the study of carbon nanotube growth mechanism by floating catalyst chemical vapor deposition for advanced composite applications", (Doctoral dissertation, Ph.D. dissertation, Dept. Eng. Mater. Sci., École Centrale Paris, Paris, France) , 2012.
- [12] Kaushik B. K. and Majumder M. K., "Carbon nanotube based VLSI interconnects: Analysis and design", New Delhi: Springer India, pp.1-14, 2015.
- [13] Maniecki T., Shtyka O., Mierczynski P., Ciesielski R., Czylkowska A., Leyko J. and Gromov D., "Carbon Nanotubes: Properties, Synthesis, and Application", Fibre Chemistry, Vol.50, No.4, pp.297-300, 2018.
- [14] Purohit R., Purohit K., Rana S., Rana R. S. and Patel V.,
  " Carbon nanotubes and their growth methods", Procedia Materials Science, No. 6, pp. 716-728, 2014.
- [15] Rahman G., Najaf Z., Mehmood A., Bilal S., Mian S. A. and Ali G., "An overview of the recent progress in the synthesis and applications of carbon nanotubes", C—Journal of Carbon Research, Vol.5, No.1, pp.3, 2019.
- [16] Li W. Z., Xie S. S., Qian L. X., Chang B. H., Zou B. S., Zhou W. Y. and Wang G., "Large-scale synthesis of aligned carbon nanotubes", Science, Vol.274, No.5293, pp. 1701-1703, 1996.

#### References

- [17] Mamalis A. G., Vogtländer L. O. G. and Markopoulos A.,
   "Nanotechnology and nanostructured materials: trends in carbon nanotubes", Precision Engineering, Vol.28, No.1, pp. 16-30, 2004.
- [18] Xia X., Chao D., Zhang Y., Zhan J., Zhong Y., Wang X. and Fan H. J., "Generic synthesis of carbon nanotube branches on metal oxide arrays exhibiting stable high-rate and long-cycle sodium-ion storage", Small, Vol.12, No.22, pp. 3048-3058, 2016.
- [19] Kumar M., "Carbon nanotube synthesis and growth mechanism", Carbon Nanotubes-Synthesis Characterization Applications, pp.147-170, 2011.
- [20] Kumar M. and Ando Y., "Chemical vapor deposition of carbon nanotubes: a review on growth mechanism and mass production", Journal of nanoscience and nanotechnology, Vol. 10, No.6, pp. 3739-3758, 2010.
- [21] Azam M. A., Manaf N. S. A., Talib E. and Bistamam M. S. A., "Aligned carbon nanotube from catalytic chemical vapor deposition technique for energy storage device: a review", Ionics, Vol.19, No.11, pp. 1455-1476, 2013.
- [22] Okubo S., Sekine T., Suzuki S., Achiba Y., Tsukagoshi K., Aoyagi Y. and Kataura H., "Purification of Single-Wall Carbon Nanotubes Synthesized from Alcohol by Catalytic Chemical Vapor Deposition", Japanese Journal of Applied Physics, Vol. 43, No. 3B, pp. 396–398, 2004.
- [23] Ferreira F. V., Cividanes L. D. S., Brito F. S., Menezes B. R. C. D., Franceschi W., Simonetti E. N. and Thim G. P., "Functionalizing Graphene and carbon nanotubes: a review", Springer, 2016.
- [24] Liu X., Wang H., Zheng Z., Liu J., Reitz R. D. and Yao M., "Development of a combined reduced primary reference fuelalcohols(methanol/ethanol/propanols/butanols/n-pentanol)

mechanism for engine applications", Energy, No. 114, pp. 542-558, 2016.

- [25] Esconjauregui S., Whelan C. M. and Maex, K., "The reasons why metals catalyze the nucleation and growth of carbon nanotubes and other carbon nanomorphologies", Carbon, Vol.47, No.3, pp. 659-669, 2009.
- [26] Bystrzejewski M., Huczko A., Byszewski P., Doman´ska M., Ru¨mmeli M. H., Gemming T. and Lange H., "Systematic Studies on Carbon Nanotubes Synthesis from Aliphatic Alcohols by the CVD Floating Catalyst Method", Fullerenes, Nanotubes and Carbon Nanostructures, 17: pp.298–307, 2009.
- [27] Szabó A., Perri C., Csató A., Giordano G., Vuono D. and Nagy J. B.,
   "Synthesis methods of carbon nanotubes and Related materials", Materials, Vol. 3, No.5, pp.3092-3140, 2010.
- [28] Sengupta J. and Jacob C., "The effect of Fe and Ni catalysts on the growth of multiwalled carbon nanotubes using chemical vapor deposition", Journal of Nanoparticle Research, Vol.12, No.2, pp. 457-465, 2010.
- [29] Firouzi A., Sobri S., Yasin F. M. and Ahmadun F., "Synthesis of carbon nanotubes by chemical vapor deposition and their application for CO<sub>2</sub> and CH<sub>4</sub> detection", In Proceedings of the 2010 International Conference on Nanotechnology and Biosensors, Hong Kong, China, Vol.2, pp. 169-172, 2011.
- [30] Abu-Abdeen M. and Aljaafari A., "Synthesis of carbon nano tubes on silicon substrates using alcohol catalytic chemical vapor deposition", Materials Sciences and Applications, Vol.2, No.07, pp. 922, 2011.
- [31] Aqel A., El-Nour K. M. A., Ammar R. A. and Al-Warthan A., "Carbon nanotubes, science and technology part (I) structure synthesis

and characterization", Arabian Journal of Chemistry, Vol. 5, No.1, pp.1-23, 2012.

- [32] Lubej M. and Plazl I., "Theoretical descriptions of carbon nanotubes synthesis in a chemical vapor deposition reactor: a review", Chemical and biochemical engineering quarterly, Vol. 26, No.3, pp. 277-284, 2012.
- [33] Dobrzańska-Danikiewicz A. D., Łukowiec D., Cichocki D. and Wolany W., "Carbon nanotubes manufacturing using the CVD equipment against the background of other methods", Archives of Materials Science and Engineering, Vol.64, No. 2, pp.103-109, 2013.
- [34] Ordoñez-Casanova E. G., Román-Aguirre M., Aguilar-Elguezabal A. and Espinosa-Magaña F., "Synthesis of carbon nanotubes of few walls using aliphatic alcohols as a carbon source", Materials, Vol. 6, No.6, pp.2534-2542, 2013.
- [35] Khorrami S. A. and Lotfi R., "Influence of carrier gas flow rate on carbon nanotubes growth by TCVD with Cu catalyst", Journal of Saudi Chemical Society, Vol.20, No.4, pp. 432-436, 2013.
- [36] Bokobza L., Bruneel J. L. and Couzi M., "Raman spectra of carbonbased materials (from graphite to carbon black) and of some silicone composites", C—Journal of Carbon Research, Vol. 1, No.1, pp.77-94, 2015.
- [37] Sharma R., Sharma A. K. and Sharma V., "Synthesis of carbon nanotubes by arc-discharge and chemical vapor deposition method with analysis of its morphology, dispersion and functionalization characteristics", Cogent Engineering, Vol.2, No.1, pp.1-7, 2015.
- [38] Granados-Martínez F. G., Contreras-Navarrete J. J., García-Ruiz D. L., Gutiérrez-García C. J., Durán-Navarro A., Gama-Ortega E. E. and Mondragón-Sánchez M. L., " MWCNTs synthesis from butanol,

diethyl ether, ethyl acetate and hexane by chemical vapor deposition with a stainless steel core as catalyst", Superficies y vacío, Vol.28, No.4, pp. 108-110, 2015.

- [39] Pandey P. and Dahiya M., "Carbon nanotubes: Types methods of preparation and applications", Carbon, Vol.1, No.4, pp.15-21, 2016.
- [40] Abdulrazzak F. H., Abbas A. M. and Hussein F. H., "Synthesis of few-wall carbon nanotubes using methanol/propanol mixture by chemical vapour deposition", Front Nanosci Nanotech, Vol.3, No.3, pp.1-7, 2017.
- [41] Tripathi N., Pavelyev V. and Islam S. S., "Synthesis of carbon nanotubes using green plant extract as catalyst: unconventional concept and its realization", Applied Nanoscience, Vol. 7, No.8, pp. 557-566, 2017.
- [42] Mirabootalebi S. O. and Akbari G., "Methods for synthesis of carbon nanotubes—review", Int. J. Bio-Inorg. Hybr. Nanomater, Vol. 6, No.2, pp. 49-57, 2017.
- [43] Manawi Y. M., Samara A., Al-Ansari T. and Atieh M. A., "A review of carbon nanomaterials' synthesis via the chemical vapor deposition (CVD) method", Materials, Vol.11, No.5, pp. 822, 2018.
- [44] Ahangarpour A., Farbod M., Ghanbarzadeh A., Moradi A. and Nafch M. A., "Optimization of Continual Production of CNTs by CVD Method using Radial Basic Function (RBF) Neural Network and the Bees Algorithm", J. Nanostructure, Vol. 8, No.3, pp. 225-231, 2018.
- [45] Shukrullah S., Naz M. Y., Mohamed N. M., Ibrahim K. A., Ghaffar A. and AbdEl-Salam N. M., "Synthesis of MWCNT Forests with Alumina-Supported Fe<sub>2</sub>O<sub>3</sub> Catalyst by Using a Floating Catalyst Chemical Vapor Deposition Technique", Journal of Nanomaterials, pp.1-12, 2019.

- [46] Dong L., Park J. G., Leonhardt B. E., Zhang S. and Liang R.,
   "Continuous Synthesis of Double-Walled Carbon Nanotubes with Water-Assisted Floating Catalyst Chemical Vapor Deposition", Nanomaterials, Vol.10, No.2, pp. 365, 2020.
- [47] Hayashi N., Honda S. I., Tsuji K., Lee K. Y., Ikuno T., Fujimoto K. and Hirao T., "Highly aligned carbon nanotube arrays fabricated by bias sputtering", Applied surface science, No.212, pp.393-396, 2003.
- [48] Lubej M. and Plazl I., "Theoretical descriptions of carbon nanotubes synthesis in a chemical vapor deposition reactor: a review", Chemical and biochemical engineering quarterly, Vol.26, No.3, pp. 277-284, 2012.
- [49] Qian C., Qi H., Gao B., Cheng Y., Qiu Q., Qin L. C. and Liu J., "Fabrication of small diameter few-walled carbon nanotubes with enhanced field emission property", Journal of nanoscience and nanotechnology, Vol. 6, No.5, pp. 1346-1349, 2006.
- [50] Grüneis A., Rümmeli M. H., Kramberger C., Barreiro A., Pichler T., Pfeiffer R. and Büchner B., "High quality double wall carbon nanotubes with a defined diameter distribution by chemical vapor deposition from alcohol", Carbon, Vol. 44, No.15, pp. 3177-3182, 2006.
- [51] Wang X., Li Q., Xie J., Jin Z., Wang J., Li Y. and Fan S., "Fabrication of ultralong and electrically uniform single-walled carbon nanotubes on clean substrates", Nano letters, Vol. 9, No.9, pp. 3137-3141, 2009.
- [52] Ganesh E. N., "Single walled and multi walled carbon nanotube structure, synthesis and applications", International journal of innovative technology and exploring engineering, Vol.2, No.4, pp. 311-320, 2013.

### References

- [53] Danish E. P. A., "Carbon nanotubes-Types, products, market and provisional assessment of the associated risks to man and the environment", Environmental project, No.1805, 2015.
- [54] Endo M., Kim Y. A., Hayashi T., Fukai Y., Oshida K., Terrones M. and Dresselhaus M. S., "Structural characterization of cup-stackedtype nanofibers with an entirely hollow core", Applied Physics Letters, Vol. 80, No.7, pp. 1267-1269, 2002.
- [55] Endo M., Kim Y. A., Ezaka M., Osada K., Yanagisawa T., Hayashi T. and Dresselhaus M. S., "Selective and efficient impregnation of metal nanoparticles on cup-stacked-type carbon nanofibers", Nano letters, Vol. 3, No.6, pp. 723-726, 2003.
- [56] Endo M., Kim Y. A., Hayashi T., Yanagisawa T., Muramatsu H., Ezaka M. and Dresselhaus M. S., "Microstructural changes induced in —stacked cupl carbon nanofibers by heat treatment ", Carbon, Vol.41, No.10, pp.1941-1947, 2003.
- [57] Zhang F., Hou P. X., Liu C. and Cheng H. M., "Epitaxial growth of single-wall carbon nanotubes", Carbon, No.102, pp.181–197, 2016.
- [58] Kalamkarov A. L., Georgiades A. V., Rokkam S. K., Veedu V. P. and Ghasemi-Nejhad M. N., "Analytical and numerical techniques to predict carbon nanotubes properties", International journal of Solids and Structures, No.43, pp.6832-6854, 2006.
- [59] kumkum S. and Sonigara B. S. ,"The wondrous world of carbon nanotubes: Structure synthesis properties and applications ", Journal of Chemical and Pharmaceutical Research , Vol.7, No.6, pp.916-933, 2015.
- [60] Patel A. M. and Joshi A. Y., "Effect of Stone-wales and Vacancy Defect in Double walled Carbon Nanotube for Mass Sensing", Procedia Technology, No.23, pp.122-129, 2016.

- [61] Dai-Li F., Yan-Hui F., Yang C., Wei L. and Xin-Xin Z., "Effects of doping Stone—Wales and vacancy defects on thermal conductivity of single-wall carbon nanotubes", Chinese Physics B, Vol. 22, No.1, pp. 1-7, 2013.
- [62] Dai X., Shen T., Chen J. and Liu H., "Effects of Defects and Doping on an Al Atom Adsorbed on Graphene: A First-Principles Investigation", Coatings, Vol.10, No.2, pp.1-8, 2020.
- [63] Kaushik B. K. and Majumder M. K., "Carbon nanotube: Properties and applications", In Carbon Nanotube Based VLSI Interconnects, Springer, New Delhi, CH.2, pp. 17-37, 2015.
- [64] Wong E. W., Sheehan P. E., and Lieber C. M., "Nanobeam mechanics: elasticity strength, and toughness of nanorods and nanotubes", Science, Vol. 277, pp. 1971-1975, 1997.
- [65] Hone J., Batlogg B., Benes Z., Johnson A. T. and Fischer J. E., "Quantized phonon spectrum of single-wall carbon nanotubes", Science, Vol.289, pp. 1730-1733, 2000.
- [66] Tans S. J., Verschueren A. R. and Dekker C., "Room-temperature transistor based on a single carbon nanotube", Nature, Vol.393, pp. 49-52, 1998.
- [67] Lehman J. H., Terrones M., Mansfield E., Hurst K. E. and Meunier,
   V. ,"Evaluating the characteristics of multiwall carbon nanotubes",
   Carbon, Vol.49, No.8, pp. 2581-2602, 2011.
- [68] Jorio A., Pimenta M. A., Souza Filho A. G., Saito R., Dresselhaus G. and Dresselhaus M. S., "Characterizing carbon nanotube samples with resonance Raman scattering", New Journal of Physics, Vol. 5, No.1, pp.1-17, 2003.
- [69] Davis V., "Investigation of dye-sensitized solar cell performance with single chirality semiconducting carbon nanotubes", Doctoral dissertation, 2015.

- [70] Ismail K. and Ismail K., "Fabrication and characterisation of SERS substrates through photo-deposition of Gold Nanoparticles", CH.1, pp.1-37, 2015.
- [71] Hodkiewicz J. and Scientific T. F., "Characterizing carbon materials with Raman spectroscopy", application note, 2010.
- [72] Kataura H., Kumazawa Y., Maniwa Y., Umezu I., Suzuki S., Ohtsuka Y. and Achiba Y., "Optical properties of single-wall carbon nanotubes", Synthetic metals, Vol. 103, No.1-3, pp. 2555-2558, 1999.
- [73] Cheng Q., Debnath S., Gregan E. and Byrne H. J., "Effects of chlorinated aromatic solvents on the dispersion of HiPco SWNTs", physica status solidi (b), Vol.245, No.10, pp. 1947-1950, 2008.
- [74] Nair N., Usrey M. L., Kim W. J., Braatz R. D. and Strano M. S., "Estimation of the (n, m) concentration distribution of single-walled carbon nanotubes from photoabsorption spectra", Analytical chemistry, Vol.78, No.22, pp.7689-7696, 2006.
- [75] Yu Z . and Brus L. , "Rayleigh and Raman scattering from individual carbon nanotube bundles", The Journal of Physical Chemistry B, Vol.105, No.6, pp. 1123-1134, 2001.
- [76] Gohil S. and Ghosh S., "Surface enhanced Raman scattering from multiwalled carbon nanotubes at low temperatures", Applied Physics Letters, Vol. 96, No.14, pp. 143108, 2010.
- [77] Ferrari A. C., Meyer J. C., Scardaci V., Casiraghi C., Lazzeri M., Mauri F.and Geim A. K., "Raman spectrum of graphene and graphene layers ", Physical review letters, Vol.97, No.18, pp. 1-4, 2006.
- [78] Maciel I. O., Anderson N., Pimenta M. A., Hartschuh A., Qian H., Terrones M. and Jorio A., "Electron and phonon renormalization near charged defects in carbon nanotubes", Nature materials, Vol.7, No.11, pp. 878-883, 2008.

### References

- [79] Fantini C., Pimenta M. A. and Strano M. S., "Two-phonon combination Raman modes in covalently functionalized single-wall carbon nanotubes", The Journal of Physical Chemistry C, Vol.112, No.34, pp. 13150-13155, 2008.
- [80] Rao R., Reppert J., Podila R., Zhang X., Rao A. M., Talapatra S. and Maruyama B., " Double resonance Raman study of disorder in CVD-grown single-walled carbon nanotubes", Carbon, Vol.49, No.4, pp.1318-1325, 2011.
- [81] Das R., Bee Abd Hamid S., Eaqub Ali M., Ramakrishna S. and Yongzhi W., "Carbon nanotubes characterization by X-ray powder diffraction–A review", Current Nanoscience, Vol.11, No.1, pp. 23-35, 2015.
- [82] García-Gutiérrez M. C., Nogales A., Hernández J. J., Rueda D. R. and Ezquerra T. A., "X-ray scattering applied to the analysis of carbon nanotubes, polymers and nanocomposites", Opt. Pura Apl., Vol.40, No.2, pp. 195-205, 2007.
- [83] Oddershede J., Nielsen K. and Stahl K., "Using X-ray powder diffraction and principal component analysis to determine structural properties for bulk samples of multiwall carbon nanotubes", Zeitschrift für Kristallographie-Crystalline Materials, Vol.222, No.(3-4), pp.186-192, 2007.
- [84] Reznik D., Olk C. H., Neumann D. A. and Copley J. R. D., "X-ray powder diffraction from carbon nanotubes and nanoparticles", Physical review B, Vol.52, No.1, pp. 116. -125, 1995.
- [85] Cao A., Xu C., Liang J., Wu D. and Wei B., "X-ray diffraction characterization on the alignment degree of carbon nanotubes", Chemical physics letters, Vol.344, No.(1-2), pp.13-17, 2001.

- [86] Zhou O., Fleming R. M., Murphy D. W., Chen C. H., Haddon R. C., Ramirez A. P. and Glarum S .H., "Defects in carbon nanostructures", Science, Vol.263, pp.1744-1747, 1994.
- [87] Saito Y., Yoshikawa T., Bandow S., Tomita M. and Hayashi T.,
  "Interlayer spacings in carbon nanotubes", "Physical Review B, Vol. 48, No.3, pp. 1907 -1909, 1993.
- [88] Suryanarayana C. and Norton M. G., "X-ray Diffraction: A Practical Approach", Springer: Berlin, 1998.
- [89] Belin T. and Epron F. , "Characterization methods of carbon nanotubes: a review", Materials Science and Engineering: B, Vol. 119, No.2, pp. 105-118, 2005.
- [90] Koch K., Bhushan B. and Barthlott W., "Multifunctional plant surfaces and smart materials", In Springer handbook of nanotechnology, Springer, Berlin, Heidelberg, pp.1399-1436, 2010.
- [91] Wang Z. and Hui C., "Electron Microscopy of Nanotube", Springer, Berlin, 2003.
- [92] Talegaonkar J. and Patil D. R. ,"Ammonia Gas Sensing Performance of Polyaniline-SnO<sub>2</sub>", International Journal of Engineering Research and Technology, Vol. 5, No. 10, 2016.
- [93] Caglar M., Ilcan S. and Caglar Y., "Influence of Substrate Temperature on Structural and Electrical Properties of ZnO Films ", J. Sci, Vol. 7, No.2, pp. 153, 2006.
- [94] Khodair Z. T., Khadom A. A. and Jasim H. A., "Corrosion protection of mild steel in different aqueous media via epoxy/ nano-material coating: preparation characterization and mathematical views", Journal of Materials Research and Technology, Vol. 8, No.1, pp.424-435, 2019.
- [95] Mote V. D., Purushotham. Y. and Dole B., "Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles",

Journal of Theoretical and Applied Physics, Vol. 6, No.3, pp.6, 2012.

- [96] Abed A. H., Khodair Z. T., Al-Saadi T. M. and Al-Dhahir T. A., "Study the evaluation of Williamson–Hall (WH) strain distribution in silver nanoparticles prepared by sol-gel method", In AIP Conference Proceedings, Vol. 2123, No. 1, pp. 020019, 2019.
- [97] Moses A., Raj E. and Nehru L. C., "Jayachandran M. and Sanjeeviraja C., "Spray pyrolysis deposition and characterization of highly (100) oriented magnesium oxide thin films", Cryst. Res. Technol., Vol. 42, No.9, pp. 867, 2007.
- [98] Belin T. and Epron F., "Characterization methods of carbon nanotubes: a review", Materials Science and Engineering: B, Vol.119, No.2, pp. 105-118, 2005.
- [99] Inkson B. J., "Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for materials characterization", In Materials characterization using nondestructive evaluation (NDE) methods, Wood-head Publishing, pp.17-43, 2016.
- [100] Kulkarni S. K., Nanotechnology: principles and practices, Springer, 2014.
- [101] Hirsch P. B., Horne R. W. and Whelan M. J., "Direct observations of the arrangement and motion of dislocations in aluminium", Philosophical Magazine, Vol.86, No.29-31, pp. 4553-4572, 2006.
- [102] Bandow S., Asaka S., Saito Y., Rao A. M., Grigorian L., Richter E. and Eklund, P. C., "Effect of the growth temperature on the diameter distribution and chirality of single-wall carbon nanotubes", Physical Review Letters, Vol.80, No. 17, pp. 3779, 1998.
- [103] Milne W. I., Teo K. B. K., Mann M., Bu I. Y. Y., Amaratunga G. A.J., De Jonge N. and Gangloff L., "Carbon nanotubes as electron

sources", physical status solidi (a), Vol. 203, No.6, pp.1058-1063, 2006.

- [104] Somani P. R., Somani S. P., and Umeno M., "Planer nanographenes from camphor by CVD", Chemical Physics Letters, Vol. 430, No. 1-3, pp. 56-59, 2006.
- [105] Zhu H., Suenaga K., Hashimoto A., Urita K., Hata K. and Iijima S.,
   "Atomic-resolution imaging of the nucleation points of single-walled carbon nanotubes", Small, Vol.1, No.12, pp. 1180-1183, 2005.
- [106] Shiue J. and Hung S. K., "A TEM phase plate loading system with loading monitoring and nano-positioning functions", Ultramicroscopy, Vol.110, No.9, pp. 1238-1242, 2010.
- [107] Pankove J. I., " Optical Process in semiconductors Dover" Publication Inc., New York, 1975.
- [108] Neamen D. A., "Semiconductor physics and devices: basic principles", New York, NY: McGraw-Hill, 2012.
- [109] Bakr N. A., Salman S. A. and Shano A. M., "Effect of Solution Molarity on Structural and Optical Properties of Nickel Oxide Thin Films Prepared by Chemical Spray Pyrolysis Technique", International Journal of Current Research, Vol.6, No.11, pp. 9644-9652, 2014.
- [110] Sahay P. P., Tewari S. and Nath R. K., " Optical and electrical studies on spray deposited ZnO thin films", Crystal Research and Technology: Journal of Experimental and Industrial Crystallography, Vol. 42, No.7, pp. 723-729, 2007.
- [111] Hoffman M., Martin S. Choi W. and Bahnemann, D.,
   "Environmental applications of semiconductor photo catalysis ", Chemical Review, Vol. 95, pp. 69-96, 1995.
- [112] Ahmed S. S., Hassan E. K. and Mohamed G. H., "Investigation of Optical Properties of NiO0.99Cu0.01 Thin Film by Thermal

Evaporation", International Journal, Vol.2, No.2, pp. 633-638, 2014.

- [113] Gao B., Bower C., Lorentzen J. D., Fleming L., Kleinhammes A., Tang X. P. and Zhou O., "Enhanced saturation lithium composition in ball-milled single-walled carbon nanotubes", Chemical Physics Letters, Vol. 327, No. 1-2, pp.69-75, 2000.
- [114] Ma R., Wei B., Xu C., Liang J. and Wu D., "Development of supercapacitors based on carbon nanotubes ", Science in China Series E: Technological Sciences, Vol. 43, No.2, pp. 178-182, 2000.
- [115] Royster Jr T. L., Chatterjee D., Paz-Pujalt G. R. and Marrese C. A.,
   "Fabrication and evaluation of thin-film solid-state sensors for hydrogen sulfide detection", Sensors and Actuators B: Chemical, Vol.53, No.3, pp. 155-162, 1998.
- [116] Hierlemann A. and Gutierrez-Osuna R., "Higher-order chemical sensing", Chemical reviews, Vol.108, No.2, pp. 563-613, 2008.
- [117] Nazeeruddin M. K., Baranoff E. and Grätzel M., "Dye-sensitized solar cells: a brief overview", Solar energy, Vol.85, No.6, pp.1172-1178, 2011.
- [118] Listorti A., O'Regan B. and Durrant J. R., " Electron transfer dynamics in dye-sensitized solar cells", Chemistry of Materials, Vol.23, No.15, pp. 3381-3399, 2011.
- [119] Assi A. A., "Conductive polymer dye sensitive solar cell (DSSC) for improving the efficiency", Doctoral dissertation, Ph. D. Thesis, University of Baghdad, 2014.
- [120] Al-Sarraf A. H. R., Khodair Z. T., Manssor M. I., Abbas R. and Shaban A. H., " Preparation and characterization of ZnO nanotripods and Nano flowers by atmospheric pressure chemical vapor

deposition (APCVD) technique", AIP Conference Proceedings 1968, pp.030005, 2018.

- [121] Saleh A. M., Bakr N. A. and Khodair Z. T., "Effect Of Oxygen Flow Rate On Structural And Optical Properties Of SnO<sub>2</sub> Thin Films Prepared By APCVD Technique", Digest Journal of Nanomaterials and Bio structures, Vol. 13, No. 3, pp. 603- 608, 2018.
- [122] Lobo L. S., "Mechanism of Catalytic CNTs Growth in 400–650° C Range: Explaining Volcano Shape Arrhenius Plot and Catalytic Synergism Using both Pt (or Pd) and Ni, Co or Fe", C—Journal of Carbon Research, Vol.5, No.3, pp. 42, 2019.
- [123] Shah K. A., Najar F. A., Andrabi S. M. A. and Islaml S. S., "Synthesis of carbon nanotubes for device applications", Asian – J Chem., No.29, pp.879–881, 2017.
- [124] Hata K., Futaba D. N., Mizuno K., Namai T., Yumura M. and Iijima, S., "Water-assisted highly efficient synthesis of impurityfree single-walled carbon nanotubes", Science, Vol.306, No.5700, pp. 1362-1364, 2004.
- [125] Ezz A. A., Kamel M. M. and Saad G. R., "Synthesis and characterization of nanocarbon having different morphological structures by chemical vapor deposition over Fe-Ni-Co-Mo/MgO catalyst", Journal of Saudi Chemical Society, Vol. 23, No.6, pp. 666-677, 2019.
- [126] José-Yacamán M., Miki-Yoshida M., Rendon L. and Santiesteban J.
   G., "Catalytic growth of carbon microtubules with fullerene structure", Applied physics letters, Vol.62, No.6, pp. 657-659, 1993.
- [127] Huang L., Wind S. J. and O'Brien S. P., "Controlled growth of single-walled carbon nanotubes from an ordered mesoporous silica template", Nano Letters, Vol. 3, No.3, pp. 299-303, 2003.

- [128] Hodkiewicz J. and Wall M., "Introduction to Raman Spectroscopy as a Characterization Tool for Carbon Nanotubes, Graphene and other Carbon Nanostructures", NSTI-Nanotech, Vol.1, pp. 318-321, 2010.
- [129] Dobrzańska-Danikiewicz A. D., Łukowiec D., Cichocki D. and Wolany W., " Carbon nanotubes manufacturing using the CVD equipment against the background of other methods", Archives of Materials Science and Engineering, Vol.64, No.2, pp. 103-109, 2013.
- [130] Ordoñez-Casanova E. G., Román-Aguirre M., Aguilar-Elguezabal A. and Espinosa-Magaña F., "Synthesis of carbon nanotubes of few walls using aliphatic alcohols as a carbon source", Materials, Vol.6, No.6, pp. 2534-2542, 2013.
- [131] Pócsik I., Hundhausen M., Koós M. and Ley L., "Origin of the D peak in the Raman spectrum of microcrystalline graphite", Journal of Non-Crystalline Solids, No.227, pp. 1083-1086, 1998.
- [132] Matthews M. J., Pimenta M. A., Dresselhaus G., Dresselhaus M. S. and Endo M., "Origin of dispersive effects of the Raman D band in carbon materials", Physical Review B, Vol.59, No.10, pp. R6585-R6588, 1999.
- [133] Thomsen C. and Reich S., "Double resonant Raman scattering in graphite", Phys. Rev. Lett., No.85, pp.5214–5217, 2000.
- Brown S. D. M., Jorio A., Dresselhaus M.S. and Dresselhaus G.,
   "Observations of the D-band feature in the Raman spectra of carbon nanotubes", Phys. Rev., Vol. 64, No.073403, pp. 1-4, 2001
- [135] Bokobza L. and Zhang J., "Raman spectroscopic characterization of multiwall carbon nanotubes and of composites", Express Polym. Lett., No. 6, pp. 601–608, 2012.

- [136] Ouyanga Y., Conga L.M., Chena L., Liub Q. X. and Fangc Y., " Raman study on single-walled carbon nanotubes an.multi-walled carbon nanotubes with different laser excitation energies", Physical E, No.40, pp. 2386–2389, 2008.
- [137] Dresselhaus M. S., Dresselhaus G. and Hofmann M., "The big picture of Raman scattering in carbon nanotubes", Vib. Spectrosc., No.45, pp. 711–781, 2007.
- [138] Zhang M. and and Li J., "Carbon nanotube in different shapes", Materials today, Vol.12, No.6, pp. 12-18, 2009.
- [139] Yuan D., Ding L., Chu H., Feng Y., McNicholas T. P. and Liu, J., " Horizontally aligned single-walled carbon nanotube on quartz from a large variety of metal catalysts", Nano letters, Vol.8, No.8, pp. 2576-2579, 2008.
- [140] Kang S. J., Kocabas C., Ozel T., Shim M., Pimparkar N., Alam M. A. and Rogers J. A., "High-performance electronics using dense, perfectly aligned arrays of single-walled carbon nanotubes", Nature nanotechnology, Vol. 2, No.4, pp. 230, 2007.
- [141] Tans S. J., Verschueren A. R. M. and Dekker C., "Room-temperature transistor based on a single carbon nanotube", Nature, Vol. 393, No.7, pp.49-52, 1998.
- [142] Kong J., Franklin N. R., Zhou C., Chapline M. G., Peng S., Cho K. and Dai H., "Nanotube molecular wires as chemical sensors", science, Vol.287, No.5453, pp. 622-625, 2000.
- [143] Misewich J. A., Martel R., Avouris P., Tsang J. C., Heinze S. and Tersoff J., " Electrically induced optical emission from a carbon nanotube FET", Science, Vol. 300, No.5620, pp.783-786, 2003.
- [144] Bachtold A., Hadley P., Nakanishi T. and Dekker C., "Logic circuits with carbon nanotube transistors", Science, Vol.294, No.5545, pp. 1317-1320, 2001.

- [145] Kong J., Soh H. T., Cassell A. M., Quate C. F. and Dai H., "Synthesis of individual single-walled carbon nanotubes on patterned silicon wafers", Nature, Vol.395, No.6705, pp.878-881, 1998.
- [146] Flahaut E., Bacsa R., Peigney A. and Laurent C., "Gram-scale CCVD synthesis of double-walled carbon nanotubes", Chemical Communications, No.12, pp. 1442-1443, 2003.
- [147] Sharma R., Sharma A. K. and Sharma V., "Synthesis of carbon nanotubes by arc-discharge and chemical vapor deposition method with analysis of its morphology, dispersion and functionalization characteristics", Cogent Engineering, Vol.2, No.1, pp. 1-10, 2015.
- [148] Hosseini A. A., Allahyari M. and Besheli S. D., "Synthesis of carbon nanotubes nano fibbers and nano union by electric arc discharge method using NaCl accuse as solution and Fe and Ni particles and catalysts", IJEST, No.1, pp. 217–229, 2012.
- [149] Hsin Y. L., Hwang K. C., Chen F. R. and Kai J. J., "Production and in-situ metal filling of carbon nanotubesin water", Advanced Materials, No.13, pp. 830–833, 2001.
- [150] Saravanan M. S. S., Babu S. P. K., Sivaprasad K. and Jagannatham, M., "Techno-economics of carbon nanotubes produced by open air arc discharge method", International Journal of Engineering, Science and Technology, Vol. 2, No. 5, pp. 100-108, 2010.
- [151] Zhu H. W., Li X. S., Jiang B., Xu C. L., Zhu Y. F., Wu D. H. and Chen X. H., "Formation of carbon nanotubes in water by the electricarc technique", Chemical Physics Letters, No. 366, pp. 664–669, 2002.
- [152] Nishimura K., Okazaki N., Pan L. and Nakayama Y., "In Situ Study of Iron Catalysts for Carbon Nanotube Growth Using X-Ray Diffraction Analysis", Japanese Journal of Applied Physics, Vol. 43, No.4, pp.471-474, 2004.

- [153] Kannaki K., Ramesh P. S. and Geetha D.," Hydrothermal synthesis of CuO Nanostructure and Their Characterizations ", International Journal of Scientific & Engineering Research, Vol. 3, No. 9, pp.1, 2012.
- [154] Kittle C. "Introduction to Solid State Physics", Eight Edition, John Wiley and Sons, pp.416, 2005.
- [155] Ali A. K. M., Al-Ajaj E. A., Al-Essa I. M., and Hassan T. A., "Fabrication of carbon nanopowder by arc discharge technique". Iraqi Journal of Physics, Vol.10, No.19, pp. 41-46, 2012.
- [156] Bari R. H., Patil1 S. B., and Bari A. R.," Synthesis, characterization and gas sensing performance of sol-gel prepared nanocrystalline SnO<sub>2</sub> thin films", International journal on smart sensing and intelligent systems, Vol. 7, No. 2, pp.610- 629, 2014.
- [157] Young S. J., Lin Z. D., Hsiao C. H. and Huang C. S., "Ethanol gas sensors composed of carbon nanotubes with adsorbed gold nanoparticles", Int. J. Electrochem. Sci, Vol. 7, No.11, pp. 11634-11640, 2012.
- [158] Roy R.K., Chowdhury M.P. and Pal A.K., "Room temperature sensor based on carbon nanotubes and nanofibres for methane detection", Vacuum, Vol. 77, pp. 223-229, 2005.
- [159] Kong J., N.R. Franklin C. Zhou M.G. Chapline S. Peng K. Cho and H. Dai, "Nanotube molecular wires as chemical sensors", Science, Vol. 287, pp. 622-625, 2000.
- [160] Barberio M., Barone P., Imbrogno A., Ruffolo S. A., La Russa M., Arcuri N. and Xu, F., "Study of dye absorption in carbon nanotubetitanium dioxide heterostructures", J. Chem. Chem. Eng, Vol.9, No.5, pp. 245-252, 2015.
- [161] Chang H, Hsieh T. J., Chen T. L., Huang K. D., Jwo C. S. and Chien S. H., " Dye-Sensitized Solar Cells Made with TiO<sub>2</sub>-Coated

Multi-Wall Carbon Nanotubes and Natural Dyes Extracted from Ipomoea", Materials Transactions, No.50, pp. 2879-2884, 2009.

- [162] Varghese O.K., Kichambre P.D., Gong D., Ong K. G., Dickey E. C. and Grimes C.A., "Gas sensing characteristics of multi-wall carbon nanotubes", Sensors and Actuators, B: Chemical, Vol. 81, pp. 32-41, 2001.
- [163] Hamid S. B. A., Tan T. L., Lai C. W. and Samsudin E. M., "Multiwalled carbon nanotube/TiO<sub>2</sub> nanocomposite as a highly active photocatalyst for photodegradation of Reactive Black 5 dye", Chinese Journal of Catalysis, Vol. 35, No.12, pp.2014-2019, 2014
- [164] Tian L., Ye, L., Deng K. and Zan L., "TiO<sub>2</sub>/carbon nanotube hybrid nanostructures: Solvothermal synthesis and their visible light photocatalytic activity", Journal of Solid State Chemistry, Vol.184, No.6, pp.1465-1471, 2011.
- [165] Wei C. H. and Chang C. M., "Polycrystalline TiO2 thin films with different thicknesses deposited on unheated substrates using RF magnetron sputtering", Materials transactions, Vol.52, No.3, pp.554-559, 2011.
- [166] Kuvarega A. T., Krause R.W. and Mamba B. B., "Nitrogen/ palladium-codoped TiO<sub>2</sub> for efficient visible light hotocatalytic dye degradation", The Journal of Physical Chemistry C, Vol. 115, No. 45, pp. 22110–22120, 2011.
- [167] Muaz A.K., Hashim U., Ibrahim F., Thong K. L., Mohktar M.S. and Liu W., "Effect of annealing temperatures on the morphology optical and electrical properties of TiO<sub>2</sub> thin films synthesized by the sol-gel method and deposited on Al/TiO<sub>2</sub>/SiO<sub>2</sub>/p-Si", Microsystem Technologies, Vol.22, No.4, pp.871-881, 2016.

- [168] Hadjoub T., Touam A., Chelouche M., Atoui J., Solard M., Chakaroun A., Fischer A., Oudrioua B. and Peng L., "Postdeposition annealing effect on RF-sputtered TiO<sub>2</sub> thin –film properties for photonic applications", Applied Physics A, Vol.122, No.2, pp.1-8, 2016.
- [169] Shirke B. S., Korake P.V., Hankare P. P., Banmane S.R. and Garadkar K.M., "Synthesie and characterization of pure anatase TiO<sub>2</sub> nanoparticales", Journal of Materials Science, Materials in Electronics, Vol.22, No.7, pp.821-824, 2011.

- **اولاً** تصنيع متحسس لغاز الايثانول، وإذ اظهرت النتائج زيادة في التحسسية عند زيادة معدل جريان الغاز.
- ثانياً تصنيع خلية شمسية صبغية DSSC، اذ تم اولاً تحميل الانابيب النانوية متعددة الجدران بنوعيه التجاري والمنتج بنسب (0.01،0.005) على ثنائي اوكسيد التيتانيوم. وذلك يترسيبها كعجينة على قاعدة زجاج FTO بطريقة شفرة الطبيب ، ومن ثم تلدينها بدرجة حرارة 450°C لمدة 30 دقيقة ، وقد تم دراسة الخواص البصرية لهذه الاغشية قبل وبعد عملية التلدين.
  - و تم الحصول على اعلى كفاءة للعينة DSSC 4 والتي بلغت 0.83%.



تم في هذه الدراسة ولأول مرة في مختبرات قسم الفيزياء – كلية العلوم – جامعة ديالى تصنيع أنابيب الكاربون النانوية متعددة الجدران (MWCNT) باستعمال منظومة الترسيب البخاري الكيميائي (CVD) والتي تم تهيأة وتصنيع اغلب اجزاءها يدوياً . اذ تم مزج نسب مختلفة من كحول الميثانول والبيوتانول باعتبارها مصدراً اساسياً للكاربون واستخدام كل من الفيروسين كعامل محفز ,وبيروكسيد الهيدروجين للنتقية.

استخدمت تقنيات مطيافية رامان والمجهر الالكتروني الماسح ذي الانبعاث المجالي(FE-SEM) ، والمجهر الالكتروني النافذ (TEM) ، وتحليل مطياف التشتت للطاقة (EDS) ، وحيود الاشعة السينية (x-ray).

G بين طيف رامان أنّ التركيب يحتوي على حزمتين رئيسيتين ولجميع العينات : وهما الحزمة G ضمن مدى  $^{-1}$  (sp<sup>2</sup>) والحزمة D عند D والتي تشير الى نمط استطالة الآصرة (sp<sup>2</sup>) والحزمة D عند المدى  $^{-1}$  (sp<sup>2</sup>) .

اظهرت صور المجهر الالكتروني (FE-SEM) تشكل الانابيب الكاربونية وبأشكال مختلفة ومنتوعة ولجميع العينات، مع نمو مستقيم الاتجاه واضح للعينات التي تم تصنيعها من مزج نسب ومتنوعة ولجميع (Methanol 50% + Butanol 50% + Butanol )، وقد كان معدل الاقطار التي تم الحصول عليها بحدود nm (200-4200).

اما صور المجهر الالكتروني (TEM) فقد اثبتت تكون انابيب الكاربون النانوية متعددة الجدران بوضوح عالي كذلك بينت تحليلات (EDS) ظهور مادة الكاربون التي تعد المادة الاساسية لتشكيل الانابيب وظهور كل من الاوكسجين والحديد.

بينت نتائج تحليلات حيود الاشعة السينية (x-ray) ان جميع العينات متعددة التبلور ومن النوع السداسي وبأتجاهية سائدة (002) .

وبعد اجراء عملية التشخيص تم استخدام العينة المنتجة من («Methanol + Butanol ) + من («Methanol ) في التطبيقات التالية وذلك بسبب النمو بالاتجاه العمودي للانابيب الكاربونية وكذلك الحصول على عينة جيدة بمقدار ((0.9 ) بعد عملية التنقية وكما يلي:-



تصنيع ودراسة الخواص الفيزيائية لأنابيب الكاربون النانوية باستخدام تقنية الترسيب الكيميائية بالبخار وبعض تطبيقاتها

أطروحة مقدمة الى كلية العلوم- جامعة ديالى و هي جزء من متطلبات نيل درجة الدكتوراه فلسفة في الفيزياء من قبل انتصار كاظم عبد أشراف

> أ.د.زياد طارق خضير 1442 هـ

أ.م.د. فراس حبيب عبد الرزاق 2020 م