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College of Science

Department of Chemistry

**SYNTHESES AND CHARACTERIZATION OF CARBON NANOTUBES PREPARED  
ON TRANSITION METALS OXIDE NANOPARTICLES**

A graduation research project

submitted to the Department of Chemistry in partial fulfillment of the requirements for the  
completion of the degree of Bachelor of Science in Chemistry

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## المستخلص:

هدف البحث لتحضير أكاسيد بعض العناصر الإنتقالية النانوية داخل فراغات أكسيد الألومنيوم كحامل لاستعمالها كمحفزات لتحضير أنابيب الكربون النانوية. تم تحضير الأكاسيد وعند فحصهـل بجهاز حيود الأشعة السينية كان حجم جسيمات المحفز الاول ، أكسيد الكوبالت، ٦٨ نانومتر والمحفز الثاني ، أكسيد الحديد مع أكسيد الألومنيوم ، ٧٤,٤ نانومتر ، والمحفز الثالث ، أكسيد الحديد مع أكسيد الألومنيوم مع اليوريا، ٦٨ نانومتر. أستعملت طريقة ترسيب البخار الكيميائي لتحضير أنابيب الكربون النانوية بنوعية جيدة وقد وصلت الحـصيلة المئوية لانابيب الكربون النانوية ٢٣١% باستعمال المحفز الثالث مما يدل على نشاط حفزي عالي جدا. اظهرت صور المجهر الألكتروني المساح لعينة أنابيب الكربون النانوية الثانية اختلافا في احجام الانابيب بحجم متوسط حوالي ٤٥ نانومتر مشوبة بالجرافيت وبقايا العامل المحفز والحامل. صور المجهر الاللكتروني النفقي لعينة انابيب الكربون الاولى ان احجامها تتراوح بين ٣١ و ٤٢,٧ نانومتر ، اما العينة الثالثة فقد كان حجمها ٣٦,٢٥ نامتر مع ظهور شوائب من الجرافيت والحافز والحامل.

## Abstract:

The research aimed to prepare some transition metal oxide nanoparticles encapsulated in aluminum oxide and to use them as catalysts for the synthesis of carbon nanotubes (CNT). The X ray diffraction (XRD) patterns showed successful preparation of the catalysts in the nano scale

size, where the size of cat. 1 ,  $\text{Co}_3\text{O}_4$  , is 68 nm, that of cat.2,  $\text{Fe}_2\text{O}_3$ , is 74.4 and cat.3 ,  $\text{Fe}_2\text{O}_3$  is 68 nm. Applying chemical vapor deposition (CVD) method for the synthesis of CNT using the prepared catalysts gave good CNT quality of the multi-walled type in the three experiments executed. The yield of CNT3, prepared by cat.3, reached 231% indicating high activity of the  $\text{Fe}_2\text{O}_3$  catalyst. The SEM images of CNT2 showed thick carbon nanotubes of about 45 nm mixed with graphite and catalyst impurities. The TEM images of CNT1 revealed a thick multi-walled CNT with a size of 31 and 42.7 nm. TEM images of CNT3 showed contamination with graphite, catalyst and supports. The size of of more than 20 concentric tubes in the each MWCNT was found to be 36.25 nm.

## CHAPTER ONE: GENERAL INTRODUCTION

### 1.1. Introduction:

Since carbon Nanotubes (CNT) were discovered by Iijima, after an arc discharge experiment in 1991, substantial researches were carried on this new material leading to uncover its marvelous properties. Investigations showed that CNT are stronger than steel, electrical conductivity higher than copper, in case of thermal conductivity and hardness it is found to have many folds higher than diamond,[1, **Mukul Kumar and Yoshinori Ando. 2010**]. Carbon nanotubes can be considered as a rolled - up graphene sheets of an in-plane  $\text{sp}^2$  hybridization. The structure of CNT is derived from a hexagonal honeycomb lattice of a seamless cylindrical shape [2 **Olk and Heremans 1994 , 3, Elton Daniel Graugnard. 2000**]

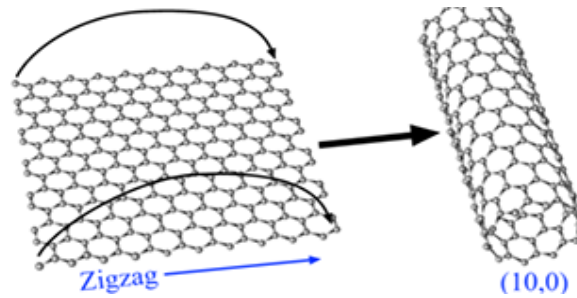


Fig. 1: Schematic representation of graphene rolling up sequence [3 Elton Daniel Graugnard. 2000].

CNT can be divided into two types according to the number of layers in the tube, single walled carbon nanotubes (SWCNT) which can has three different forms according to the way of rolling up of the graphene sheet to a cylinder, these forms are zigzag, chiral, and armchair. Multi walled nanotubes (MWNCTs) are concentric single walled nanotubes of increasing diameter. The material properties of MWNCTs are mostly dependent upon the perfection and orientation of the graphitic planes comprising the MWNCT[2 Olk and Heremans 1994]. CNT possesses an attractive chemical, physical and mechanical properties over the known bulk materials used in daily life, this can be attributed to the nano scale size of CNT and hybridization pattern.

CNT can be prepared by using different method by applying heat to diverse types organic precursors in gas , liquid or solid forms under inert gas atmosphere. Three main techniques are widely used , the first one is the arc-discharge by which Iijima produced and characterized CNT for the first time. The second one is the laser-ablation technique, these two methods require very high energy. The third and the most popular method is the chemical vapor deposition (CVD), it gain its popularity from that it require relatively low temperature, ease of usage and the possibility of scaling up to mass production [4, Ali Eatemadi 2014].

## 1.2. Objectives of the study

The objective of this research is to prepare different transition metals nanoparticles and to use them as catalysts for the syntheses of carbon nanotubes (CNT) , and to characterize the catalyst nanoparticles and the synthesized CNT.

## CHAPTER TWO

### LITERATURE REVEIW

#### **2.1. Types of Carbon Nanotubes (CNT):**

Carbon Nanotubes, long, thin cylinders of carbon, were discovered in 1991 by Sumio Iijima. These are large macromolecules that are unique for their size, shape, and remarkable physical properties. They can be thought of as a sheet of graphite (a hexagonal lattice of carbon) rolled into a cylinder. These intriguing structures have sparked much excitement in recent years and a large amount of research has been dedicated to their understanding. Currently, the physical properties are still being discovered and disputed. Nanotubes have a very broad range of electronic, thermal, and structural properties that change depending on the different kinds of nanotube (defined by its diameter, length, and chirality, or twist). To make things more interesting, besides having a single cylindrical wall (SWNTs), Nanotubes can have multiple walls (MWNTs)--cylinders inside the other cylinders.[ 5] **Chris Scoville, et al** ,[6]**Valentin N. Popov**,[7] **Marc Monthieux, et al ]**

### **2.1.1. Single Walled Carbon Nanotubes (SWCNT):**

Geometrically, there is no restriction on the tube diameter. However, calculations have shown that collapsing the single-wall tube into a flattened two-layer ribbon is energetically more favorable than maintaining the tubular morphology beyond a diameter value of  $\approx 2.5$  nm. On the other hand, it is easy to grasp intuitively that the shorter the radius of curvature, the higher the stress and the energetic cost, although for the synthesis (thermal gradients, residence time, and so on), Experimental data are consistent with these statements, since SWNTs wider than 2.5 nm are only rarely reported in the literature, whatever the preparation method, while the length of the SWNTs can be in the micrometer or the millimeter range. These features make single-wall carbon nanotubes a unique example of single molecules with huge aspect ratios. [ 5] **Chris Scoville, et al** ,[6]**Valentin N. Popov**,[7] **Marc Monthieux, et al** ]

### **2.1.2. Multi Walled Carbon Nanotubes (MWCNTs):**

Building multiwall carbon nanotubes is a little bit more complex, since it involves the various ways that graphenes can be displayed and mutually arranged within filamentary morphology. A similar versatility can be expected to the usual textural versatility of polyaromatic solids. Likewise, their diffraction patterns are difficult to differentiate from those of anisotropic polyaromatic solids. The easiest MWCNT to imagine is the concentric type (c-MWCNT), in which SWCNTs with regularly increasing diameters are coaxially arranged (according to a Russian-doll model) into a multiwall nanotube. Such nanotubes are generally formed either by the electric arc technique (without the need for a catalyst), by catalyst-enhanced thermal cracking of gaseous hydrocarbons, or by CO disproportionation . [ 5] **Chris Scoville, et al** ,[6]**Valentin N. Popov**,[7] **Marc Monthieux, et al** ]

## **2.2. Properties of CNT:**

The electronic properties of CNT as a conductor or a semiconductor depends largely upon their geometrical characteristics, so they are incorporated in many devices such as electronic circuits, field emission devices. The thermal properties of CNT are outstanding exceeding that of copper metal. Their mechanical properties dominate that of steel with several orders of magnitude, this property renders CNT as strongest fiber ever known till date.



CNT were used in many useful applications replacing the ordinary materials with successful results. Examples of these applications are applications in fields such as electron field emission, sensors, probing tips, lithium batteries hydrogen storage and mechanical reinforcements as composite filling due to their high tensile strength and low density [8 Zhang, X. , et al. 2003].

### **2.2.1. Structural and Thermal Properties of SWNTs:**

The stability of CNT is governed by the diameter. The reason that the most frequent diameter is  $\approx 1.4$  nm is again a matter of energy balance. Single-wall nanotubes larger than  $\approx 2.5$  nm are not stable. On the other hand, the strain on the C–C bond increases as the radius of curvature decreases. The optimal diameter (1.4 nm) should therefore correspond to the best energetic compromise. [9 Carbon Nanotube: Properties and Applications.

[file:///C:/Users/ASUS/Downloads/9788132220466-c2%20\(5\).pdf](file:///C:/Users/ASUS/Downloads/9788132220466-c2%20(5).pdf) ]

The diameters of SWNT-type carbon nanotubes fall in the nanometer regime, but SWNTs can be hundreds of micrometers long. SWNTs are narrower in diameter than the thinnest line that can be obtained in electron beam lithography. SWNTs are stable up to 750 °C in air (but they are usually damaged before this temperature is reached due to oxidation mechanisms, as demonstrated by the fact that they can be filled with molecules. They are stable up to  $\approx 1500$ –1800 °C in inert atmosphere, beyond which they transform into regular, polyaromatic solids. They have half the mass density of aluminum. The properties of a SWNT, like any molecule, are heavily influenced by the way that its atoms are arranged. The physical and chemical behavior of a SWNT is therefore related to its unique structural features. [9 Carbon Nanotube: Properties and Applications.

[file:///C:/Users/ASUS/Downloads/9788132220466-c2%20\(5\).pdf](file:///C:/Users/ASUS/Downloads/9788132220466-c2%20(5).pdf) ]

### **2.2.2. Adsorption Properties of SWNTs:**

An interesting feature of a SWNT is that it has the highest surface area of any molecule due to the fact that a graphene sheet is probably the only example of a sheet like molecule that is energetically stable under normal conditions. If we consider an isolated SWNT with one open end (achieved through oxidation treatment for instance), the surface area is equal to that of a single, flat graphene sheet:  $\approx 2700$  m<sup>2</sup>/g (accounting for both sides). In reality, nanotubes –

specifically SWNTs – are usually associated with other nanotubes in bundles, fibers, films, papers, and so on, rather than as a single entity. Each of these associations has a specific range of porosities that determines its adsorption properties (this topic is also covered in on applications). [ 9 ]

### **2.2.3. Electronic and Optical Properties:**

The electronic states in SWNTs are strongly influenced by their one-dimensional cylindrical structures. One-dimensional subbands are formed that have strong singularities in the density of states (Van Hove singularities) . By rolling the graphene sheet to form a tube, new periodic boundary conditions are imposed on the electronic wave functions, which give rise to one-dimensional subbands:  $C_n K = 2q$  where  $q$  is an integer.  $C_n$  is the roll-up vector  $na_1 + ma_2$  which defines the helicity (chirality) and the diameter of the tube. Much of the electronic band structure of CNTs can be derived from the electronic band structure of graphene by applying the periodic boundary conditions of the tube under consideration. [ 6 Valintena ,7 Marc et al ]

### **2.2.4. Mechanical Properties:**

While tubular nanomorphology is also observed for many two-dimensional solids, carbon nanotubes are unique due to the particularly strong bonding between the carbons ( $sp^2$  hybridization of the atomic orbitals) of the curved graphene sheet, which is stronger than in diamond ( $sp^3$  hybridization), as revealed by the difference in C–C bond lengths (0.142 versus 0.154 nm for graphene and diamond respectively). This makes carbon nanotubes – SWNTs or c-MWNTs – particularly stable against deformations. The tensile strength of SWNTs can be 20 times that of steel and has actually been measured as  $\approx 45$  GPa. Very high tensile strength values are also expected for ideal (defect-free) c-MWNTs, since combining perfect tubes concentrically is not supposed to be detrimental to the overall tube strength, provided the tube ends are well capped (otherwise, concentric tubes could glide relative to each other, inducing high strain). [6 Valintena ,7 Marc et al ]

### **2.2.5. Reactivity:**

The chemical reactivities of graphite, fullerenes, and carbon nanotubes are similar in many ways. Like any small object, carbon nanotubes have a large surface to interact with their environment .

It is worth noting, however, that nanotube chemistry differs from that observed for regular polyaromatic carbon materials due to the unique shape of the nanotube, its small diameter, and its structural properties. Unlike graphite, perfect SWNTs have no (chemically active) dangling bonds (the reactions of polyaromatic solids is known to occur mainly at graphene edges). Unlike fullerenes, the ratio of weak sites (C–C bonds involved in heterocycles) to strong sites (C–C bonds between regular hexagons) is only deviates slightly from 0 for ideal tubes. [ 6 Valintena ,7 Marc et al ]

### **2.3. Methods of CNT syntheses:**

Producing carbon nanotubes so that the currently planned applications become marketable will require solving some problems that are more or less restrictive depending on the case. Examples include specifically controlling the configuration (chirality), the purity, or the structural quality of CNT, and adapting the production capacity to the application. One objective would be to understand the mechanism of nanotube nucleation and growth perfectly, and this remains a controversial subject despite an intense, worldwide experimental effort. This problem is partly due to our lack of knowledge regarding several parameters controlling the conditions during synthesis. For instance, the exact and accurate role of the catalysts in nanotube growth is often unknown. Given the large number of experimental parameters and considering the large range of conditions that the synthesis techniques correspond to, it is quite legitimate to think of more than one mechanism intervening during nanotube formation. [9] **Carbon Nanotube: Properties and Applications.** ] , [ 10] **Paul L. McEuen<sup>1</sup> , Michael Fuhrer<sup>2</sup> , and Hongkun Park<sup>3</sup>. The most common CNT synthesis techniques are the followings:**

#### **2.3.1. Arc discharge method:**

A chamber containing a graphite cathode and anode contains evaporated carbon molecules in a buffer gas such as helium. The chamber also contains some amount of metal catalyst particles (such as cobalt, nickel, and/or iron). DC current is passed through the chamber while the chamber is also pressurized and heated to ~4000K. In the course of this procedure, about half of the evaporated carbon solidifies on the cathode tip into a "cylindrical hard deposit." The remaining carbon condenses into "chamber soot" around the walls of the chamber and "cathode soot" on the cathode. The cathode soot and chamber soot yield either single-walled or multi-

walled carbon nanotubes. The cylindrical hard deposit doesn't yield anything particularly interesting. [ 9,10]

### **2.3.2. Laser ablation method:**

A quartz tube containing a block of graphite is heated in a furnace. A flow of argon gas is maintained throughout the reaction. A laser is used to vaporize the graphite within the quartz. The carbon vaporizes, is carried away by the argon, and condenses downstream on the cooler walls of the quartz. This condensation is SWNT and metallic particles. Thereafter, purification methods are applied to this mixture. The key to the proper formation of the condensed nanotubes is that the location where the carbon atoms begin to condense should be set up as a curved sheet of graphene with a catalyst metallic atom nearby. As carbon atoms begin to attach and form rings, the metallic atom, if it has the proper electronegativity properties, will preserve the open edge of the tube and prevent it from drawing to a close. [ 9,10 ]

### **2.3.3: Chemical vapor deposition:**

From last twenty years, carbon fibers and filaments are produced using chemical vapor deposition of hydrocarbons along with a metal catalyst. In this process, large amount of CNTs is produced by catalytic CVD of acetylene over cobalt and iron. Using the carbon/ zeolite catalyst, fullerenes and bundles of SWNTs can be produced along with the MWNTs. Lot of research works have been carried out for the formation of SWNTs/MWNTs from ethylene that is supported by the catalysts such as iron, cobalt, and nickel. The recent research works have also demonstrated the production of SWNTs and DWNTs on molybdenum and molybdenum–iron alloy catalysts. A thin alumina template with or without nickel catalyst is achieved using the CVD of carbon within the pores. Ethylene can be used with reaction temperatures of 545 °C for Nickel catalyzed CVD and 900 °C for an uncatalyzed process that produces carbon nanostructures with open ends . Methane can also be used as carbon source for synthesization. Catalytic decomposition of H<sub>2</sub>/CH<sub>4</sub> mixture over cobalt, nickel, and iron is used to obtain high yields of SWNTs at 1,000 °C. The usage of H<sub>2</sub>/CH<sub>4</sub> atmosphere between a non-reducible oxide such as Al<sub>2</sub>O<sub>3</sub> or MgAl<sub>2</sub>O<sub>4</sub> and one or more transition metal oxides can produce the composite powders containing well-dispersed CNTs. Thus, higher proportions of SWNTs and lower

proportions of MWNTs can be achieved using the decomposition of CH<sub>4</sub> over the freshly formed nanoparticles. [ 9,10 ]

#### **2.4. Preparation of transition metals nanoparticles oxides (TMNO) catalysts:**

Catalytic studies using transition - metal NP catalysts became popular in the second half of the twentieth century with a small but important group of reactions, namely hydrogenation, hydro silylation and hydration of unsaturated organic substrates and redox reactions including water photo splitting and photocatalytic hydrogenation. [ 11] **HONGJIE DAI**, [12] **Transition - metal Nanoparticles**]

For synthesizing CNTs, typically, nanometer-size metal particles are required to enable hydrocarbon decomposition at a lower temperature than the spontaneous decomposition temperature of the hydrocarbon. Most commonly-used metals are Fe, Co, Ni, because of two main reasons:

- (i) high solubility of carbon in these metals at high temperatures
- (ii) high carbon diffusion rate in these metals. Besides that, high melting point and low equilibrium vapor

Solid organometallocenes (ferrocene, cobaltocene, nickelocene) are also widely used as a CNT catalyst, because they liberate metal nanoparticles in-situ which catalyze the hydrocarbon decomposition more efficiently.

particle size dictates the tube diameter. Hence, metal nanoparticles of controlled size, presynthesized by other reliable techniques, can be used to grow CNTs of controlled diameter. Thin films of catalyst coated on various substrates are also proven good in getting uniform CNT deposits (Fan et al., 1999). The key to get pure CNTs is achieving hydrocarbon decomposition on the catalyst surface alone and prohibiting the aerial pyrolysis In 2008, *gigas growth* of CNT was reported from Fe-Co catalyst on zeolite support resulting in a weight gain of 1000% and volume gain of 10,000%, relative to the zeolite bed. Hence, by combining different metals in different ratios and carefully controlling the catalyst calcination conditions, it is possible to evolve new crystallographic phases that could exhibit much higher catalytic activity toward CNT growth. Very recently, highly active crystallographic phases of Co-Mo and Ni-Mo have been achieved on MgO support, yielding ~3000 wt% CNT growth .

Recent developments in the nanomaterials synthesis and characterization have enabled many new catalysts for the CNT growth. Apart from popularly used transition metals (Fe,Co, Ni), a range of other metals (Cu, Pt, Pd, Mn, Mo, Cr, Sn, Au, Mg, Al) has also been successfully used for horizontally-aligned SWCNT growth on quartz substrates .[1]

### **2.5. Purification of CNT:**

As-produced carbon nanotubes are intrinsically inert, often aggregated or entangled, and may contain impurities (such as amorphous carbon or catalytic metal particles and supports) . The purification processes that have been investigated usually utilize the differences in the aspect ratio and oxidation rate between the CNTs and impurities . A post-synthesis treatment is almost always required to purify and disperse the CNTs in a suitable solvent; a wide variety of approaches have been developed. A typical strategy is to use thermal oxidation, then acid reflux in concentrated HCl, and finally a thermal annealing treatment to purify the raw material; a surfactant can subsequently be used to disperse the CNTs using sonication . A small concentration of dissolved ethyl cellulose, for example, can be added to MWNTs/isopropyl alcohol solution to disperse the CNTs when preparing stable suspensions for electrophoretic deposition of CNTs . However, residual surfactants can be difficult to remove once added and may be detrimental to the performance of the nanotubes in a given application . Alternatively, a mixture of concentrated nitric and sulphuric acids can simultaneously purify, shorten and functionalise CNTs . [ 11,12 ]

### **2.6. Supports of Transition Metals Oxide Nanoparticles:**

The performance of metal particles in catalytic reactions is governed by their size and shape as well as by interactions with the oxide support.

The same catalyst works differently on different support materials. Commonly used support substrates in CVD are quartz, silicon, silicon carbide, silica, alumina, alumino-silicate (zeolite), CaCO<sub>3</sub>, magnesium oxide, etc. For an efficient CNT growth, the catalyst-substrate interaction should be investigated with utmost attention. Metal–substrate reaction (chemical bond formation) would cease the catalytic behavior of the metal. Alumina materials are reportedly a better catalyst support than silica owing to stronger metal support interaction in the former, which allows high metal dispersion and thus a high density of catalytic sites. Such interactions

prevent metal species from aggregating and forming unwanted large clusters that lead to graphite particles or defective MWCNTs. Recent in-situ XPS analysis of CNT growth from different precursors on iron catalyst supported on alumina and silica substrates have confirmed these theoretical assumptions. Thin Alumina flakes (0.04–4  $\mu\text{m}$  thick) loaded with iron nanoparticles have shown high yields of aligned CNTs of high aspect ratio. [13] Mukul Kumar. 2011.

## **2.7. Organic substrates:**

Most commonly used CNT precursors are methane, ethylene, acetylene, benzene, xylene and carbon monoxide. Among the early reports of CVD, MWCNTs were grown from the pyrolysis of benzene at 1100°C and from acetylene at 700°C. In those cases, iron nanoparticles were used as the catalyst. Later, SWCNTs were also produced from benzene, acetylene, ethylene, methane, cyclohexane, fullerene etc. by using various catalysts. Low temperature synthesis of high-purity SWCNTs was reported from alcohol CVD on Fe-Co impregnated zeolite support, vertically-aligned SWCNTs were also grown on Mo-Co-coated quartz and silicon substrates (Murakami et al., 2004). Recently, it has been shown that intermittent supply of acetylene in ethanol CVD significantly assists ethanol in preserving the catalyst's activity and thus enhances the CNT growth rate. Linear hydrocarbons such as methane, ethylene, acetylene, thermally decompose into atomic carbons or linear dimers/ trimers of carbon, and generally produce straight and hollow CNTs. On the other hand, cyclic hydrocarbons such as benzene, xylene, cyclohexane, fullerene, produce relatively curved/hunched CNTs with the tube walls often bridged inside.[13]

## **2.8.SEM and TEM as tools for Characterization of CNT:**

Scanning (SEM) and transmission (TEM) Electron microscopy are an imaging techniques that use an electron beam in order to probe a material. Since the wavelength of an electron is much smaller than the wavelength of visible light, diffraction effects occur at much smaller physical dimensions. The microscope was the first tool by means of which a real study could be made of objects too small to be seen with the naked eye. The modern microscope is an instrument that approaches the "theoretical limit" of its performance, the information that can be extracted from High Resolution Transmission Electron Microscopy (HRTEM) is not straight-forward since the preparation of TEM samples may mask some observation of CNTs arrangements. A great variety of experiments has been carefully done to give the properties of the atoms, molecules, electrons,

protons... regarded as the constituents of matter. The limitation on the performance of a microscope is set by its resolving power. Further characterization tools are desirable especially those which are not destructive for the samples to complete electron microscopy studies. [11,12 ]

## **2.9. Applications of CNT:**

CNT gain an exciting properties that make it a wonder between other materials. Among these properties is that it is 100 times stronger than steel and six times lighter than it, harder and more heat resisting than diamond, electrical conductance thousand times more than copper and can be a semiconductor ,high thermal stability up to 4000 °C, in addition to high surface area and the ability to chemical functionalization.

According to these unusual properties, many applications of CNT were now proposed to replace the ordinary bulk materials. CNT can be applied as reinforcing materials for many composites, in nano electronic circuits, optical uses, biomedicine, biosensor and many other applications [14 Morad, et al , 2012]].

### **Some applications of CNTs in medicine are as follows:**

Carrier for Drug delivery: Carbon nanohorns (CNHs) are the spherical aggregates of CNTs with irregular horn like shape. Research studies have proved CNTs and CNHs as a potential carrier for drug delivery system . Artificial implants, Normally body shows rejection reaction for implants with the post administration pain but, miniature sized nanotubes and nanohorns get attached with other proteins and amino acids avoiding rejection. Preservative, Carbon nanotubes and nanohorns are antioxidant in nature. Diagnostic tool, Protein-encapsulated or protein/enzyme filled nanotubes, due to their fluorescence ability in presence of specific biomolecules have been tried as implantable biosensors. As catalyst, Nanohorns offer large surface area and hence, the catalyst at molecular level can be incorporated into nanotubes in large amount and simultaneously can be released in required rate at particular time.

As Biosensors, CNTs act as sensing materials in pressure, flow, thermal, gas, optical, mass, position, stress, strain, chemical, and biological sensors. [[15] KalpnaVarshney, 2014]



## CHAPTER THREE

### MATERIALS AND METHODS

#### 3.1. Preparation of Transition Metal Oxides Nanoparticles:

##### 3.1.1. Preparation of cobalt oxide nanoparticles on aluminum oxide support

###### (Co<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>):(Cat. 1)

Calculated mass of cobalt acetate tetra hydrate (98.5%, LOBA chemie, india) was weighed and dissolved in 40 ml of methanol (AR, BDH), 3.0 grams of calcined Al<sub>2</sub>O<sub>3</sub> were added to it to give a ratio of 5% of Co encapsulated in Al<sub>2</sub>O<sub>3</sub>, then, the suspension was stirred with magnetic stirrer for one hour at 600 round per minute. The mixture was evaporated on a hot plate in the hood until drying. The dry cake was collected and ground in agate mortar and calcined in a porcelain evaporating dish in the muffle furnace at 600 °C for 3 hours, cooled and ground again and preserved in a plastic container for characterization and CNT synthesis.

##### 3.1.2. Preparation of iron oxide nanoparticles on aluminum oxide support (Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) :

###### (Cat. 2)

Calculated mass of iron(II) sulphate hepta hydrate AR. (99.0%, BDH) was weighed and dissolved in 40 ml of methanol (AR, BDH), 3 grams of calcined Al<sub>2</sub>O<sub>3</sub> were added to it to give a ratio of 5% of Fe encapsulated in Al<sub>2</sub>O<sub>3</sub>, (Fe: Al<sub>2</sub>O<sub>3</sub>) and the suspension was stirred with magnetic stirrer for one hour at 600 round per minute. The mixture was evaporated on a hot plate in the hood until drying. The dry cake was collected and ground in agate mortar and calcined in a porcelain evaporating dish in the muffle furnace at 600 °C for 3 hours, cooled and ground again and preserved in a plastic tube for characterization.

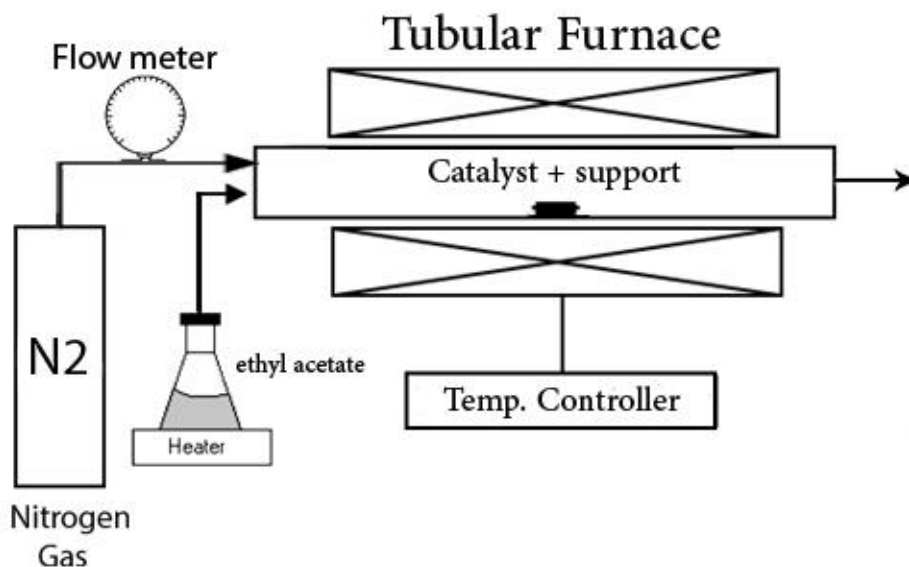
##### 3.1.3. Preparation of iron oxide nanoparticles on calcined aluminum oxide support with urea fuel (Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/ urea), (Cat. 3):

Calculated mass of iron(II) sulphate hepta hydrate AR. (99.0%, BDH) was weighed and dissolved in 40 ml of methanol (AR, BDH), 5.0 grams of urea were dissolved in the methanolic solution, then 3.0 grams of calcined Al<sub>2</sub>O<sub>3</sub> were suspended in the solution to give a ratio of 5.0 % of Fe encapsulated in Al<sub>2</sub>O<sub>3</sub>, (Fe: Al<sub>2</sub>O<sub>3</sub>) . The suspension was stirred with the magnetic stirrer

for one hour at 600 round per minute. The mixture was evaporated on a hot plate in the hood until drying. The dry cake was collected and ground in agate mortar and calcined in a porcelain evaporating dish in the muffle furnace at 600 °C for 3 hours, the fluffy brown product was cooled and ground again and preserved in a plastic container for characterization and CNT synthesis.

### **3.2. Synthesis of CNT by Catalytic Chemical Vapor Deposition (CCVD):**

The catalytic Chemical Vapor Deposition (CVD) technique was followed in the preparation of CNT. 0.2 gram of each catalyst ( Cat. 1, Cat. 2 and Cat. 3) was weighed in a dry porcelain boat and evenly spread at the bottom and inner sides of the boat and placed in a furnace reactor ( Nabertherm 1100 °C) made of a heater and stainless steel cylinder of 800 mm in length and 40 mm inner diameter. The exhaust joint was attached to the SS cylinder and connected to the fume hood. 40 liter / hour nitrogen gas current was allowed to flow through the cylinder while the temperature of the furnace was increased gradually at a rate of 20 °C / minute to the reaction temperature at 700 °C. When the temperature reached about 550 °C, the 500 ml Pyrex glass conical flask containing 40 ml of pure ethanol was heated to boil gradually on a hotplate, when the temperature of the furnace reached 700 °C, the ethanol vapor was carried by the current of the nitrogen gas to the reaction zone in the SS cylinder at a rate of 2 ml of / minute. All the 40 ml of ethanol were evaporated in about 20 minutes and entered to the reaction zone to grow the CNT on the catalyst and the support in the boat. After all ethanol evaporated, the reaction was allowed at 700 °C for further 20 minutes, the ethanol vapor valve was closed and the empty flask was removed and the reaction temperature started to decrease gradually under the nitrogen gas current until it reached 250 °C, then the nitrogen flow was stopped and the boat and its content were allowed to cool to the room temp. The boat and its content were removed from the furnace SS cylinder, the catalyst, support and the black CNT were removed in a weighed plastic container and the total mass and the CNT yield was determined for each catalyst as shown in table 1.



**Fig. 2: Schematic diagram of the CVD reactor used for CNT synthesis.**

### 3.3 . Purification of CNT:

The crude CNT were purified by boiling in 30 ml of concentrated hydrochloric acid for 30 minutes, allowed to stay for 24 hours then filtered under water suction using Buchner apparatus . The filter paper was washed with distilled water until free of the acid, then dried at 80 °C for 6 hours in the oven, collected and preserved in plastic container for further characterization.

### 3.4. Characterization of TMON by XRD:

Cat.1 , Cat. 2 and Cat. 3 were characterized by X- Ray Diffraction technique using ..... instrument , model ..... as in fig. 3,4 and 5.

### 3.5. Characterization of CNT by SEM and TEM:

CNT2 was characterized by scanning electron microscopy SEM ( model JEOL ..... ) the results were shown in figure 7a and 7b.

CNT1 and CNT3 were imaged using transmission electron microscopy (TEM) model ..... , the results were shown in fig. 8a and 8b and fig. 9a , 9b and 9c.

## CHAPTER FOUR

### RESULTS AND DISCUSSION

#### 4.1. Characterization of metal oxide nanoparticles catalysts by XRD:

A catalyst of nano particle size is the key step for the successful synthesis of CNT. The XRD pattern of Cat.1 reveals peaks belonging to the  $\text{Co}_3\text{O}_4$  at  $2\theta$  angle around **26**, 36, 43.3, 53 and 57 . Applying Scherer formula to the most intense peaks approximates the size of catalysts particles at 68 nm as in fig. 3. **R.K. Gupta et al 2011** prepared  $\text{Co}_3\text{O}_4$  at 400 and 950  $^{\circ}\text{C}$ , he found that the  $\text{Co}_3\text{O}_4$  was crystallized in a single spinal phase and a size of 15nm and 85 nm by Scherer formula, the XRD pattern in this research were in good agreement with his XRD peaks .

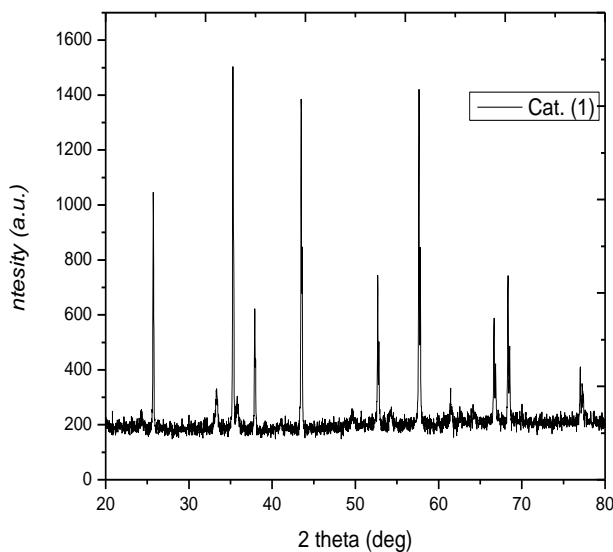


Fig. 3: **XRD pattern of Cat. 1,  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  pattern.**

**Scherrer equation ; size in nanometer nm =  $(K \lambda / \beta \cos\theta)$  X (180/3.14)**

( $K= 0.9$ ,  $\lambda= 0.15406$  nm  $\beta =$  calculated from the intense peak ,  $\cos\theta =$  half of the  $2\theta$  of the intense peak. [16 R.K. Gupta 2011])

Cat.2 showed peaks of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in the XRD pattern, the calculated particle size from the intense peaks was found to be around 74.4 nm as in fig. 4.

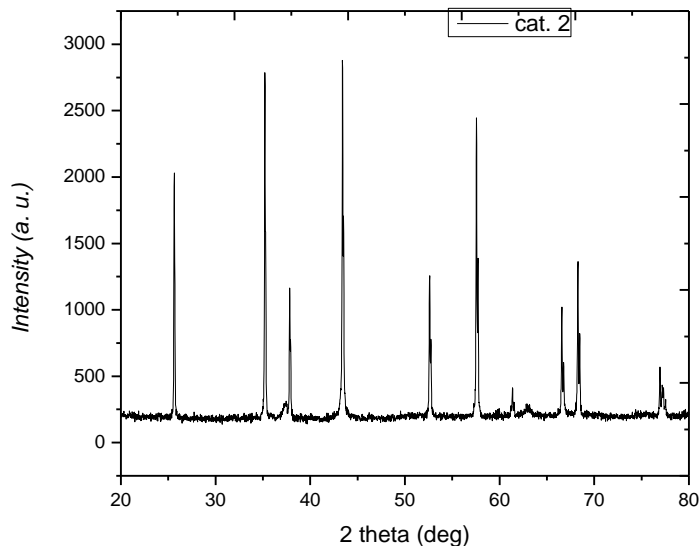
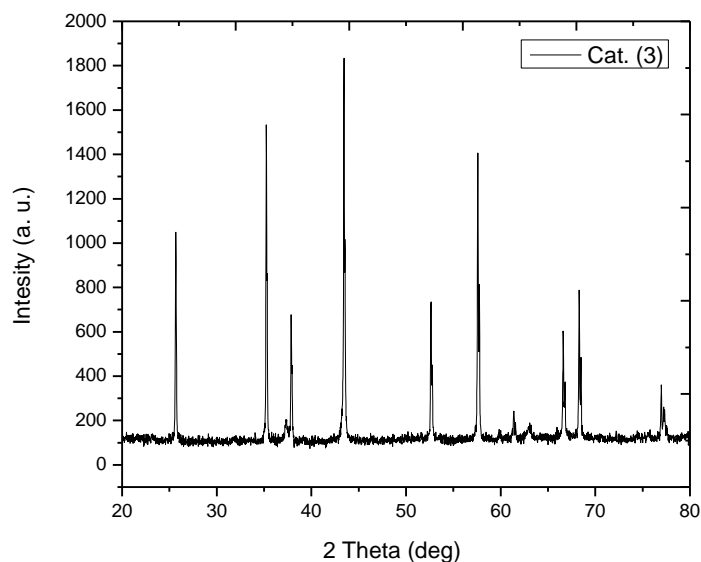


Fig. 4: **XRD pattern of Cat. 2:  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$**

Peaks of cat.3 ( $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{urea}$ ) appear on the patterns in fig. 5. The peaks related to  $\text{Fe}_2\text{O}_3$  and its resulting oxides appear at  $2\theta^0$  around 43.4, 35, 57, 26, and 53, the particle size was found to be 68 nm, as in Fig. 5.



**Fig. 5: XRD pattern of Cat.3:Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/Urea**

#### 4.2. Yield of CNT:

The low production yield is the one of the most critical limitation facing the publicity of CNT utilization in the different applications[... ] . Preparation of an active catalyst capable of multiplying the yield is considered as a target for many research groups to decrease the high cost. As seen from the table below, the iron oxide , Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/ Urea , Cat.3 , gave the highest yield , 231.4%, this catalyst can be considered as a promising one for reduction of the cost and maximizing the yield.

$$\% \text{ Yield of CNT} = \text{mass of CNT} \times 100\% / \text{mass of the catalyst}$$

table 1: CNT yield percent from the three catalysts.

| <b>Cat. No.</b> | <b>Cat. composition</b>  | <b>Mass of CNT<br/>gram</b> | <b>% Yield of CNT</b> |
|-----------------|--|-----------------------------|-----------------------|
| <b>Cat. 1</b>   | <b>Co/Al<sub>2</sub>O<sub>3</sub></b>                                | <b>0.1531</b>               | <b>78.0 %</b>         |
| <b>Cat. 2</b>   | <b>Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub></b>       | <b>0.2100</b>               | <b>101.0%</b>         |
| <b>Cat. 3</b>   | <b>Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/ Urea</b> | <b>0.6432</b>               | <b>231.40%</b>        |

#### 4.3. Characterization of CNT:

### 4.3.1. XRD of CNT2:

The XRD pattern of CNT2 showed the characteristic graphite and carbon nanotubes peaks at  $2\theta$  equals  $27^\circ$  and  $43.3^\circ$ . Also the pattern showed the presence of the  $\text{Al}_2\text{O}_3$  support even after the concentrated hydrochloric acid purification as in fig. 6.

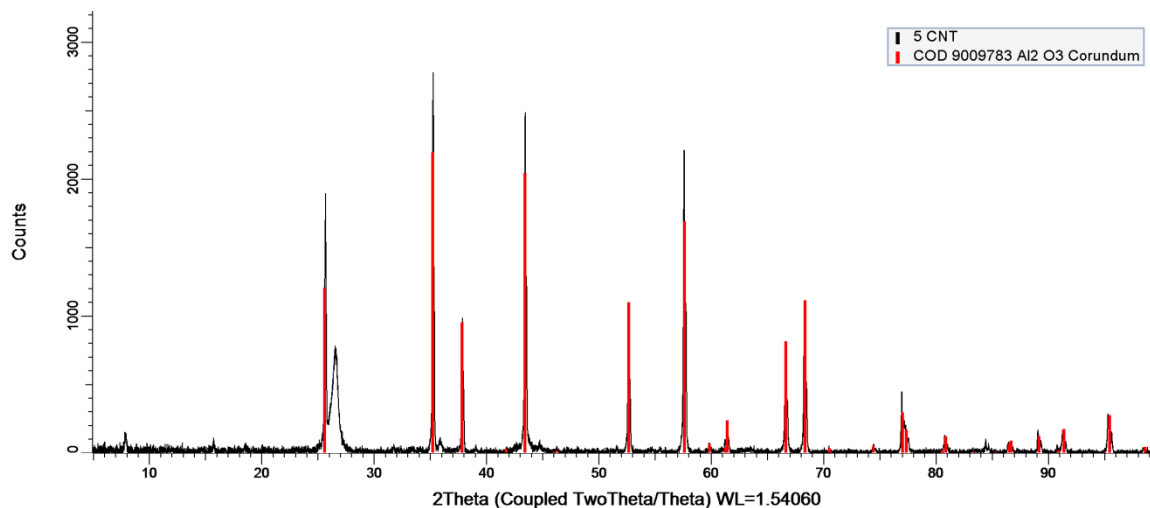


Fig. 6: XRD pattern of CNT2:

The SEM image of the CNT2 showed the successful preparation of very thick and long multi-walled carbon nanotubes (MWCNT), with granular graphite and support as an impurities. This showed that the CNT produced need further purification with oxidizing agents to get rid of the accompanying graphite and catalyst and supports as in fig. 7a and 7b.

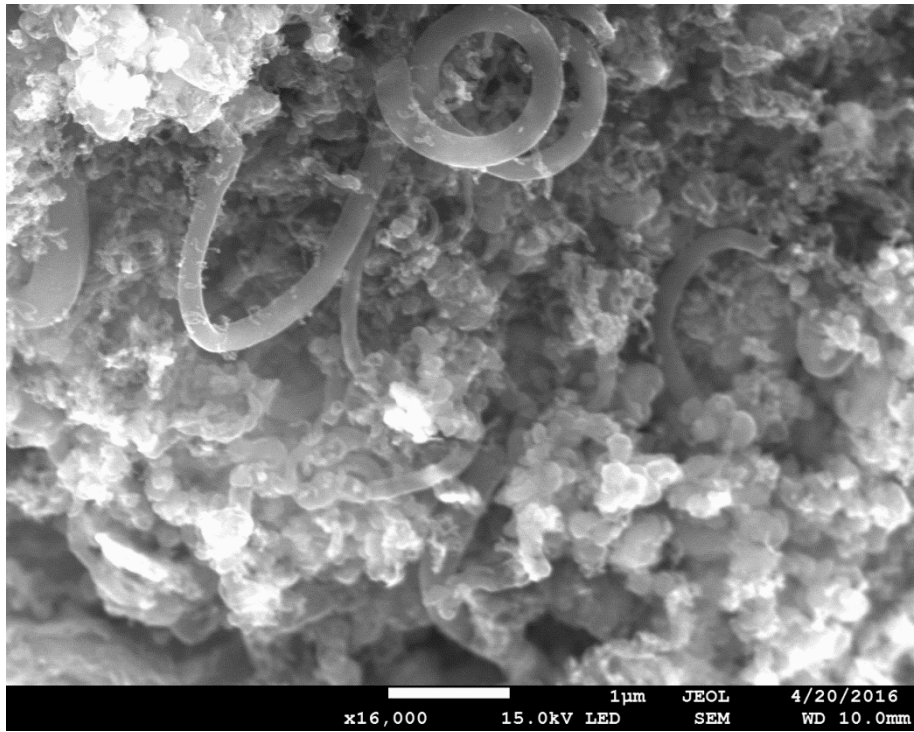


Fig. 7a: SEM images of CNT2

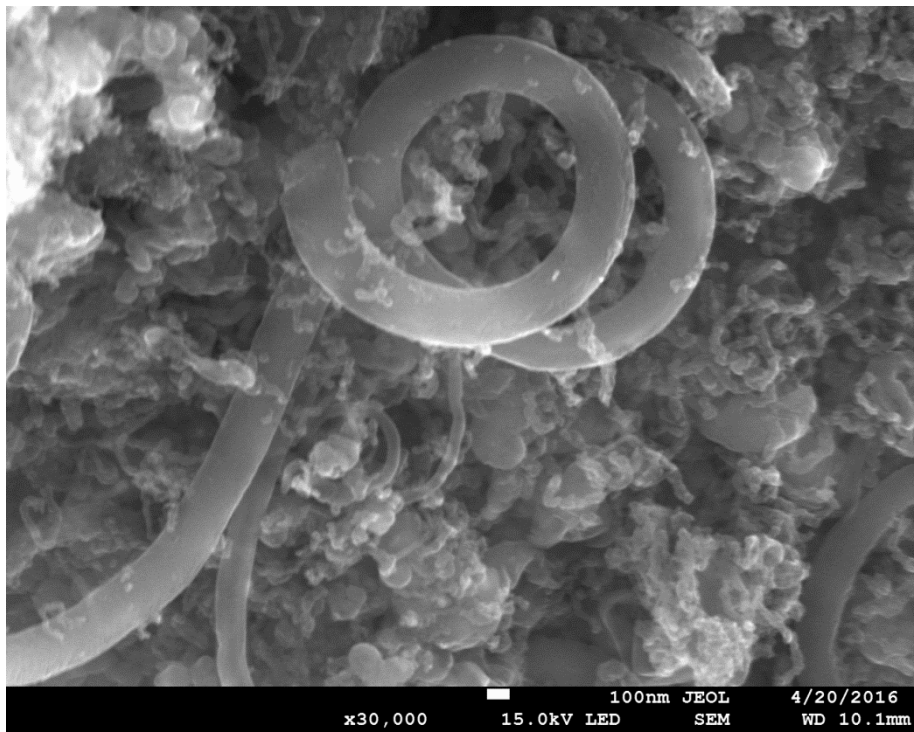


Fig. 7b: SEM images of CNT2



#### 4.3.2. Characterization of CNT2 by TEM:

TEM images of CNT2 confirmed that, the multi-walled CNT were prepared by  $\text{Fe}_2\text{O}_3$  nanoparticles as a catalyst. The size of the MWCNT was 31nm and 42.7 nm. The TEM images again confirmed the presence of graphite and catalyst as impurities in the CNT as in fig. 8a and 8b.

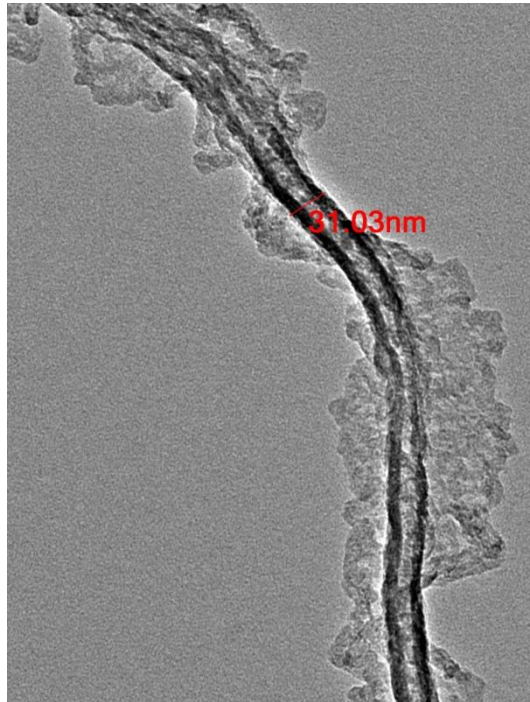


Fig. 8a: TEM images of CNT1 at 100nm imaging.

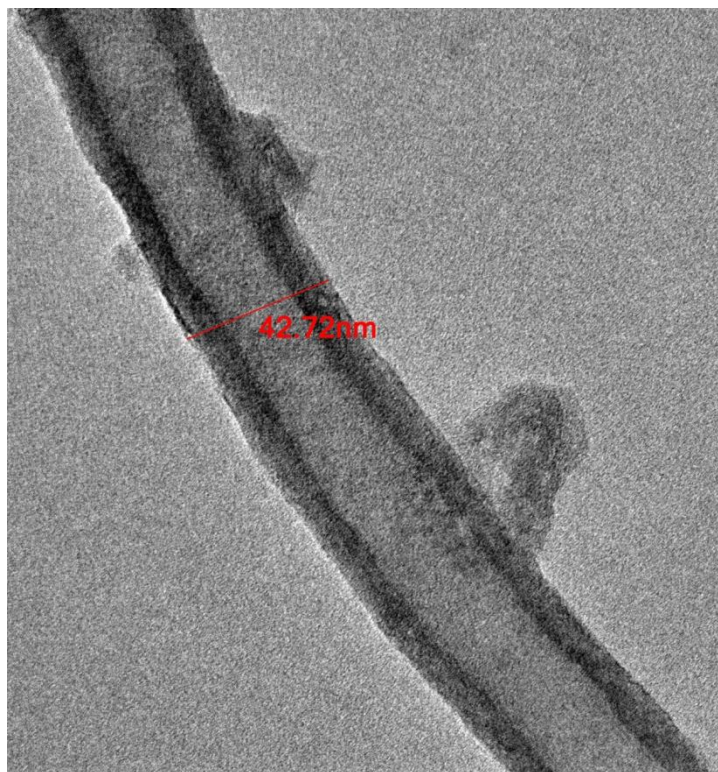


Fig. 8b: TEM images of CNT1 at 20 nm imaging.

#### **4.3.3. Characterization of CNT3 by TEM:**

The TEM images of CNT3 , prepared by  $\text{Fe}_2\text{O}_3$  nanoparticles with urea fuel showed different ( 36.25 nm and a variable range of impurities as in fig. 9a and 9b. The concentric multi-walled CNT were clearly seen in fig. 9c where more than 20 concentric carbon nanotubes were seen.



Fig. 9a: TEM images of CNT3

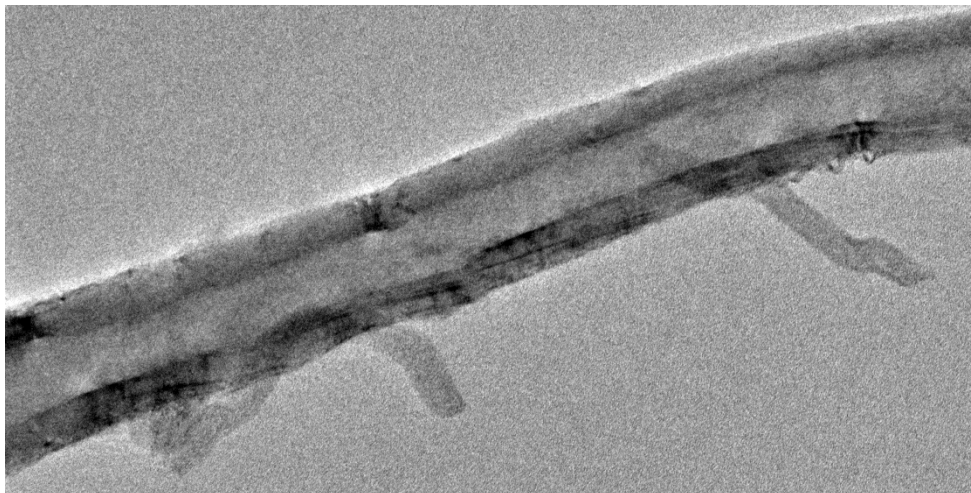


Fig. 9a: TEM images of CNT3at 50 nm imaging.

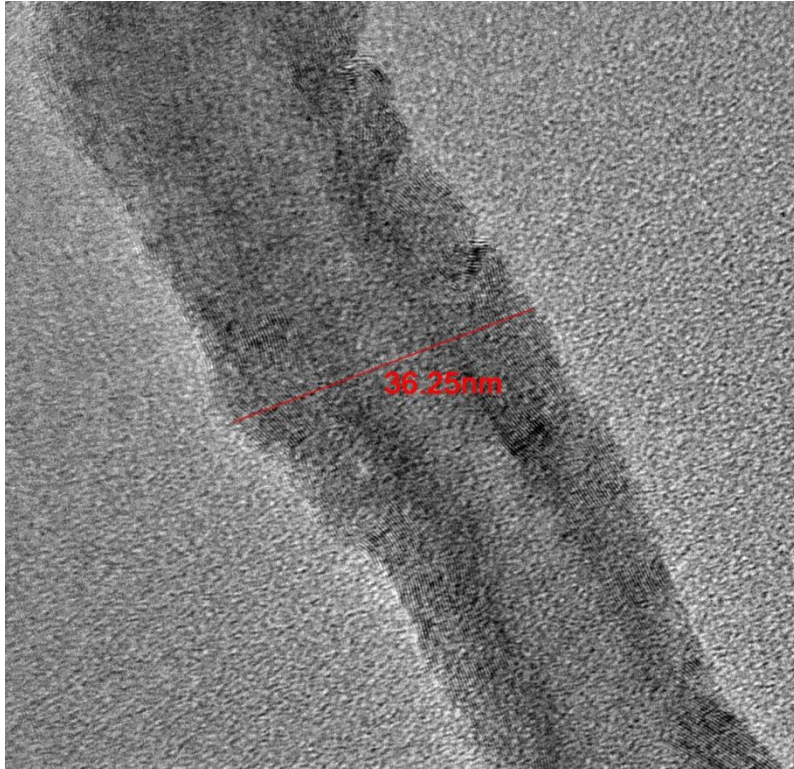


Fig. 9b: TEM images of CNT3at 10 nm imaging.

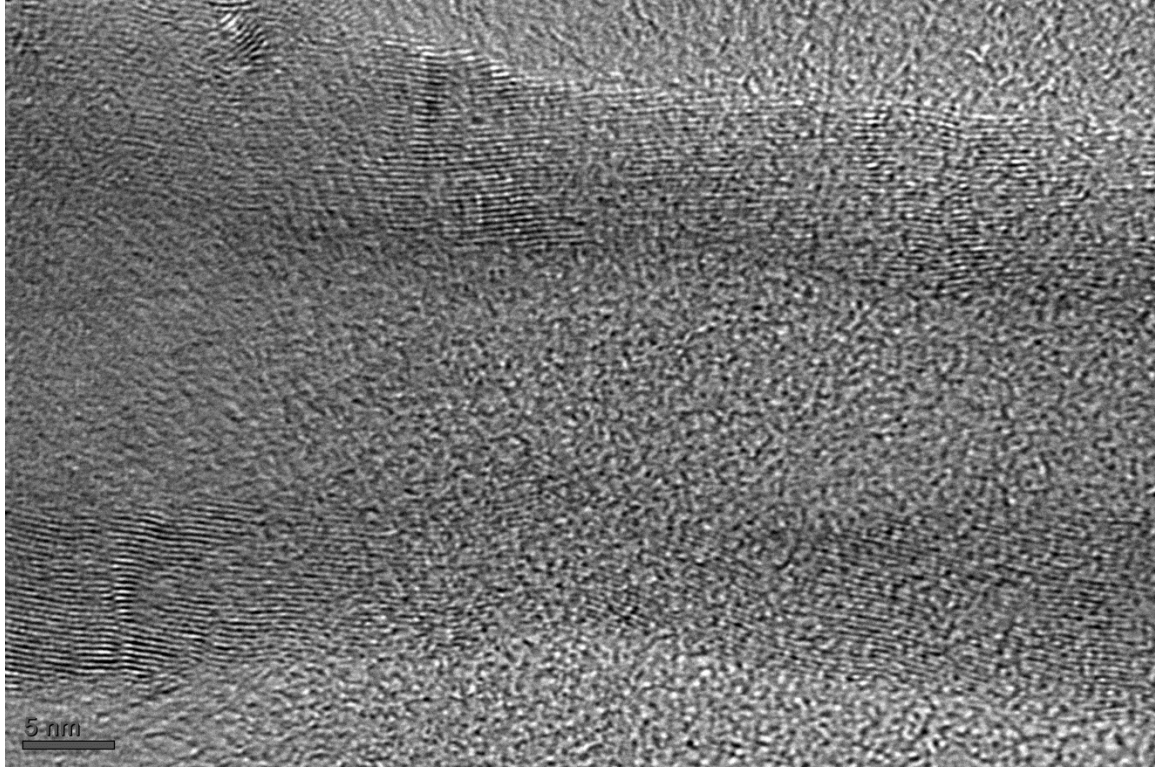


Fig. 9c: TEM images of CNT3 at 5 nm imaging.



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