Synthesis of Fe-CNTs Nanocomposite and Its Ignition with Photo Flash

A Thesis Submitted to the Department of Chemical Engineering, School of Chemical and Materials Engineering (SCME), NUST, Islamabad, in the partial fulfillment of the requirements for the degree of

Masters of Science (MS)

In

Energetic Materials Engineering

Submitted by

Saleem Shah

Registratio Number: NUST201260677MSCME67612F

Supervisor: Dr. Abdul Qadeer Malik

Co - Supervisor: Dr. Habib Nasir

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST)

H-12 Campus Islamabad

October 2014

Certificate

It is certified that the entire work in the thesis i.e. “Synthesis of CNTs-Fe Composite as a Nano Energetic Material (nEM) and Its Initiation by Photo Flashing” by Mr. Saleem Shah, for award of MS degree in Energetic Material Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan; is an original work completed in the presence of my guidance and supervision. Research work is authentic and fulfill the required criteria of MS.

Supervisor: _______________

Dr. Abdul Qadeer Malik
School of Chemical and Materials
Engineering, NUST Islamabad.

Co-Supervisor:____________

Dr. Habib Nasir
School of Chemical and Materials
Engineering, NUST Islamabad.

Submitted through

Principal/Dean: _______________

School of Chemical and Materials Engineering NUST Islamabad.

Dedication

Dedicated to my loving parents, respected teachers, friends and to my colleagues.

Acknowledgements

All Commendations to **Almighty Allah**, the most Beneficent, the most Merciful, Who blessed me with intellect, resoluteness and determination to accomplish this research project. All the respects to His Holy Prophet Hazrat Muhammad (PBUH), who enabled us to recognize our creator. I wish to extend my sincere gratitude to my able supervisors Dr. Habib Nasir and Dr. AQ malik, for giving me an opportunity to work under their supervision and providing guidance throughout the study. They have been the source of inspiration and their support, encouragement, and comments have been of greatest help. I would like to thank my GEC members Dr. Muhammad Bilal Khan Niazi and Dr. Iram Mehmood for their guidance, suggestions and encouragement. I also extend my special thanks to Dr. Abdul Mateen (IST) for helping me to accomplish my research. I would like to thank Dr. Muhammad Mujahid, Dr. Arshad Hussain and Col. Nadeem Ehsan for their support and encouragement. I also extend my gratitude to Pakistan Army in general and Pakistan Army Ordnance Corps in particular for detailing me to undergo MS (Energetic Materials Engineering) from SCME (NUST). I also pay my thanks to my respected friends and colleagues, Maj Fahad, Maj Farrukh and Maj Imran who were always there to encourage and appreciate my work. I also applaud the nice company of my all class fellows. I always cherish the happy moments spent with them. I pay my homage, sweet sensation of love and respect to my family, especially my parents who taught me the value of hard work and provided me enormous support all my life. It would not have been easy without their encouragement, cooperation and prayers.

(Saleem Shah)

Table of Contents

List of Figures

List of Tables

List of Acronyms

1-D (One Dimensional)

CNTs (Carbon nanotubes)

CVD (Chemical Vapour Deposition)

DTA (Differential Thermal Analysis)

DWCNTs (Double Walled Carbon nanotubes)

EDS (Energy Dispersive Spectroscopy)

FE-SEM (Field Emission Scanning Electron Microscopy)

FTIR (Fourier Transform Infrared Spectroscopy)

MWCNTs (Multi Walled Carbon nanotubes)

nEM (Nano Energetic Material)

SCCM (Standard Cubic Centimetres per Minute)

SWCNTs (Single Walled Carbon nanotubes)

TGA (Thermogravometric Analysis)

wt (wt.)

X-RD (X-Ray Diffraction)

Abstract

In this study a Fe-CNTs Nanocomposite was synthesised by exploiting the excellent adsorption abilities of CNTs through doping with Fe nanoparticles and ignition of the composite was achieved by subjecting it to camera photo flash. During synthesis process the raw or as received MWCNTs were purified and activated by grafting these tubes through wet oxidation process with OH and COOH functional groups. The activated CNTs were decorated with Fe nanoparticles in different concentrations. Samples were characterized by using FTIR, FE-SEM, EDS, TG/DTA and XRD techniques. It was found that photo flash ignition of CNTs-Fe composite was attained with minimum doping of 15.89 % Fe particles by weight (wt.) and maximum ignition efficiency was achieved with 32.22 % Fe. Two important aspects of this study were; Fe nanoparticles were decorated on CNTs without getting pre mature oxidation of these metal particles in air and also avoiding their agglomeration, being well dispersed on CNTs surfaces. Secondly, CNTs which are thermally very stable species got ignited by applying flashes of a simple photo camera with intensity of 14 mW/cm^2. Fe-CNTs displayed its decomposition around 350 ^{o}C instead of 600 ^{o}C as compared to the degradation of pristine CNTs. Same synthesis technique may be used for adsorbing various nanometals on the surface of CNTs for their further application as sorbents.

Keywords: Nanocomposite, CNTs, Doping, Fe, Photo Flashing.

Chapter 1: Introduction

1. *This chapter deals with the types, properties and synthesis techniques of Carbon Nanotubes, purpose of research work and its study in relation to various steps followed during practical approaches is also highlighted.*

1.1. Carbon Nanotubes (CNTs)

CNTs are one dimensional (1-D) Nano species and they may have diameter less than 1 nm up to 50 nm but length can be of several centimetres. Since their discovery in 1991 these tubes have become one of the strongest candidates for future device applications due to unique electrical, mechanical and thermal properties [1]. CNTs may be envisioned as a rolled single sheet of graphene but differing in thickness, length and in number of layers making their electrical characteristics difference by acting as conductors or semi conductors.

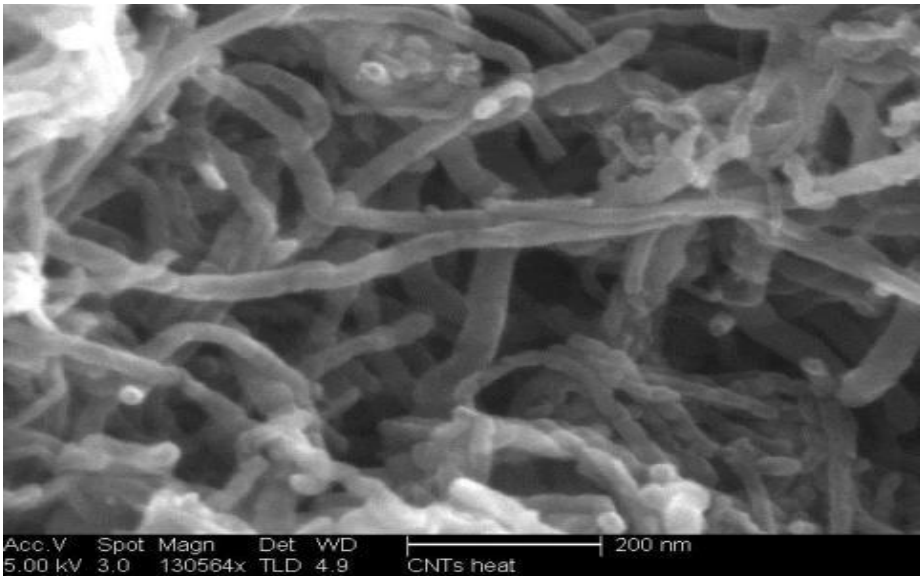


Figure 1.1: CNTs images at 200 nm scale.

1.1.1. Types of CNTs

There are three main categories in which CNTs are classified i.e. Single Walled Carbon Nanotubes (SWCNTs), Double Walled Carbon Nanotubes (DWCNTs) and Multi Walled Carbon Nanotubes (MWCNTs).

SWCNTs is conceptualized by rolling up of single graphene sheet into a seamless cylinder and this wrapping is shown by a pair of indices i.e. (n, m). The integers n and m denote the number of unit vectors along two directions in the honey comb crystal lattice of graphene. If $m = 0$, the nanotubes are called zigzag nanotubes, and if $n = m$, the nanotubes are called arm chair nanotubes. Otherwise, they are called chiral.

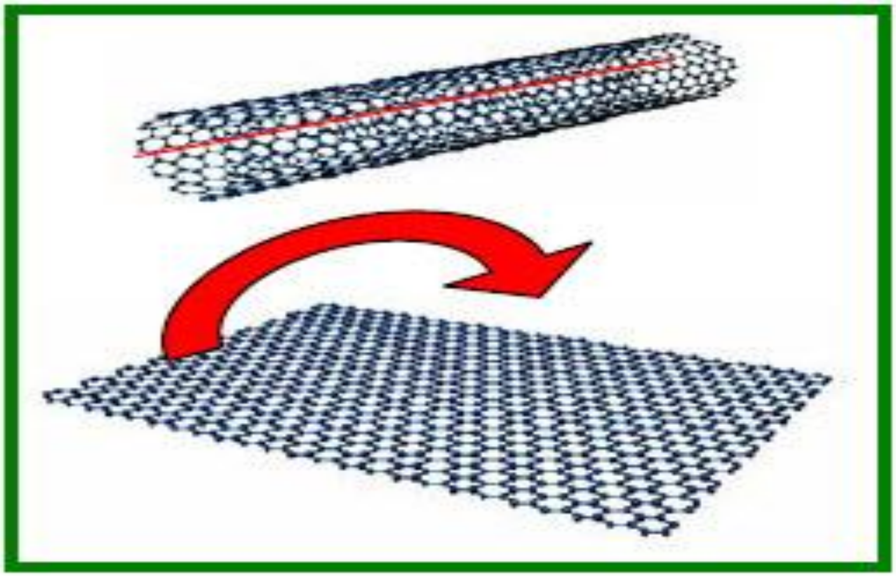


Figure 1.2: Structure of SWCNTs.

DWCNTs are a special type of nanotubes as their properties and morphology are similar to those of SWCNTs but resistance to chemicals is significantly improved. This plays an important role when activation/functionalization of CNTs is required in order to achieve tubes of specific properties. Thus only the outer wall is modified by breaking some of C=C double bonds leaving holes in the structure of nanotubes, which will not change its electrical and mechanical properties DWCNTs as much as it is done is SWCNTs.

MWCNTs consist of more than two concentric tubes of rolled graphene sheets. The distance between tubes surfaces is approximately the same as distance between the graphene layers in graphite i.e. 3.4 A^o [2, 3].

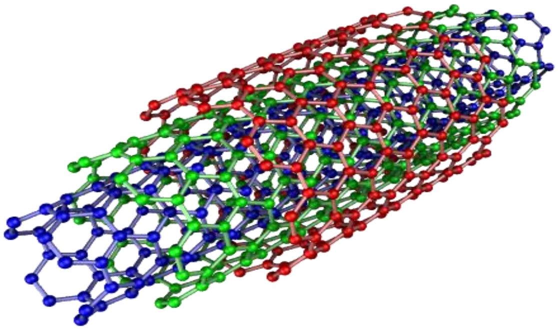


Figure 1.3: Structure of MWCNTs.

1.1.2. Properties of CNTs

The inherent mechanical, Kinetic, Electrical and Thermal properties of CNTs make them the very distinguish Nano material. Over all CNTs exhibit very unique combination of these properties as compared to other fibre materials which usually lack one or more of these properties. Here only some of the important properties including few defects of this class of species are highlighted in the subsequent paragraphs.

1.1.2.1. Mechanical Strength

CNTs are the stiffest and strongest materials in terms of elastic modulus and strength. This is due to the covalent bonds formed in between the individual carbon atoms. MWCNTs are supposed to have 63 GPa tensile strength. This means that these tubes have the ability to endure 6422 kg wt. on a cable of 1 mm^2 cross section area but these tubes may under go plastic strain under excessive tensile strain. However individual tube exhibits extremely high strength but lower shear interactions among adjacent tubes causes significant decrease in the effective mechanical strength to few GPa. This issue was recently addressed by cross linking of inner tubes by high energy electrons irradiation and increasing the strength up to 60 GPa and 17 GPa for MWCNTs and DWCNTs respectively [4].

1.1.2.2. Kinetic Properties

MWCNTs are various concentric nanotubes, accurately nested with in one another and thus the inner core tube can slide without any friction. This creates an atomic rotational and linear bearing. This is a precise positioning of atoms to make a Nano machine in the field of molecular nanotechnology. The same property was utilized to invent the smallest rotational motor[5].

1.1.2.3. Electrical Properties

Due to symmetry and unique electronic structure of graphene, the nanotubes strongly affect their electrical properties. For a given (n, m) nanotube, if $n = m$, the nanotube is metallic, if $n - m$ is a multiple of 3, then the nanotube is semi conducting with a very small band gap, other wise the Nano tube is a moderate semi conductor. Thus all arm chair ($n = m$) nanotubes are metallic, and nanotubes (6, 4), (9, 1), etc. are semi conducting. However this rule has exceptions, because curvature effects in small diameter tubes can strongly influence electrical properties. Thus a (5, 0) SWCNT should be semi conducting in fact is metallic according to the calculations. In theory the metallic nanotubes can carry an electric current density of 4×10^9 A/cm^2, which is more than 1,000 times greater than those of metals such as copper. However electrons only migrate along tube’s axis due to Nano scale cross section, as a result, CNTs are frequently referred to as 1-D conductors [6, 7].

1.1.2.4. Thermal Properties

All CNTs are said to be very good thermal conductors along the tube axis and exhibit Ballistic Conduction but good insulators laterally. MWCNTs are indeed ballistic conductors at room temperature over many microns [8]. At room temperature SWCNTs have the conductivity of about $3500\ \mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ where as copper which is known as good conductor has the conductivity of about $385\ \mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ and have the conductivity of 1.52 $W \cdot m^{-1} \cdot K^{-1}$ in the radial direction, which is about as thermally conductive as soil. The temperature stability of CNTs is estimated to be up to about 750 ^{o}C in air and 2800 ^{o}C in vacuum [9, 10].

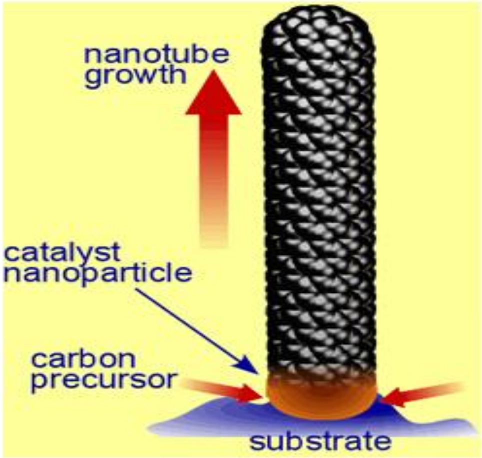
1.1.2.5. Defects

In CNTs defects may occur in the form of atomic vacancies and such defects can lower up to 85% the tensile strength. Due to the very small structure of CNTs, its tensile strength depends on its weakest segment in a similar manner to a chain, where the strength of the weakest link becomes the maximum strength of the chain. Crystallographic defects also affect the tube's electrical properties. A common result is lowered conductivity through the defective region of the tube. A defect in arm chair type tubes (which can conduct electricity) can cause the surrounding region to become semi conducting, and single mono atomic vacancies induce magnetic properties. Crystallographic defects strongly affect the tube's thermal properties. Such defects lead to phonon scattering, which in turn increases the relaxation rate of the phonons. This reduces the mean free path and reduces the thermal conductivity of nanotube structures [11].

1.1.3. Synthesis Techniques of CNTs

By Arch Discharge method carbon is contained in the negative electrode where it is sublimated due to high discharge temperature. 30% yield by wt. is achieved and both SWCNTs and MWCNTs can be produced. In Laser Ablation technique a graphite target is vaporized by pulse laser in a high temperature reactor and an inert gas is inserted in to chamber. nanotubes are developed on the cooler surface of reactor by condensing the carbon vapours. 70% yield may be achieved and primarily SWCNTs are produced with a controlled diameter. Same conditions as of arch discharge and laser ablation are applied in the Plasma Torch method, except carbon containing gas is used instead of graphite vapour to produce CNTs. This technique is more efficient and also occurs at low cost and it is a continues process. During Chemical Vapour Deposition (CVD) a layer of metal catalyst particles i.e. Iron, Cobalt, Nickel or combination is prepared on a catalyst support (substrate) such as Al_2O_3 or MgO to enhance the surface area to produce higher yield.

The size of metal particles directly affects the diameter of nanotubes. The substrate is heated to the range of 700 ^{o}C and N_2 and H_2 are introduced into the reactor as process gas. The carbon containing gas e.g. ethylene or ethanol is decomposed at the sites of catalyst particles. CVD is the most commonly used technique.



Chemical Vapor Deposition. On the surface of the catalyst, the carbon-based gas breaks apart. From there, the nanotube grows outwards from the surface.

Figure 1.4: CVD technique.

1.2. Purpose of Study

Nanotechnology has potential to boost the economic growth of a country, as in 2000 the US government took an initiative for setting up the National Nanotechnology Department and since then investment in the country has grown annually. In the current era most commercial achievements have been made possible from the incorporation of Nano materials into composites in order to achieve the most desired results. More recently CNTs have been explored with its unique chemistry and properties as well as greater volume to size ratio and readiness to convert these tubes into hybrid nanocomposite material, has brought this species into the spot light for future applications. Keeping in mind the afore said characteristics of CNTs, this research project was conceived in order to synthesise a nanocomposite material by doping of CNTs with Iron nanoparticles to achieve Fe-CNTs composite. In addition to that photo flashing effects on the nanocomposite were also probed out. Moreover, to analyse the final product through different analytical techniques and to probe out its thermal, kinetic, chemical and physical nature also come under this project umbrella. Important features of this study are discussed briefly in the following paragraphs.

1.2.1. Basis of Thesis

Under mentioned characteristics of CNTs formed the basis and inspiration for taking up of this research work. These aspects are summarized as;

- In CNTs the heat accumulation is faster than dissipation due to the nature of 1-D structure so that more drastic increase in temperature is anticipated.
- Ignition in CNTs is found to be due to agitated oxidation of Nanometal catalyst particles like Fe or Ni, exposed in air upon flashing. If these particles are dispersed sparsely the heat generated by Fe–O reaction is insignificant and ignition of neighbouring CNTs appears to be unlikely.
- So the amount of catalyst particles plays a key role for ignition. The content of catalyst to trigger CNTs ignition must be 14% to 30% by wt. [12].
- Since MWCNTs have higher thermal conductivity as compared to SWCNTs thus the ability to dissipate the heat required for ignition more readily exists in it. Therefore it is expected that SWCNTs are more likely to ignite.
- Addition of a suitable oxidant i.e. $NaClO_4$ may provide sufficient amount of oxygen to CNTs and metal (Fe) in the nanocomposite for their complete oxidation [13].

1.2.2. Probing the Photo Flashing Effects on CNTs

In recent years various research work has been done on the photo ignition and acoustic effect of CNTs by exposing these to single or multiple light flashes. As it is clear that phenomena of photo flashing attributes to the photo acoustic effect; light emitted by camera flash is absorbed by CNTs and same energy is transferred into vibrational energy, causing localised heating of the nanotube lattice. Critical to this phenomena is the rapid increase in temperature of some of the sites on tubes surface or we may say localized hot spots are generated due to the presence of residual Nanometal particles in the CNTs. Being 1-D Nano material in nature and slow heat dissipation in CNTs than accumulation causes to ignite the tubes by oxidation of metal Nanoparticles.

It has been proven that local temperature produced by oxidation of SWCNTs was in the range of 1500 – 2000 ^{o}C, causing initiation of conventional energetic material. Hence, it basically happened due the presence of hot sites generated by camera photo flashing [14]. One of the important factors in addition to the role of residual metal Nanoparticles is played by the density of nanotubes; less dense CNTs get ignited more readily as compared to highly compact or dense tubes by applying camera photo flashing [12].

1.2.3. Purification and Activation of CNTs

CNTs produced through existing techniques mostly contain impurities such as amorphous carbons, catalyst particles and graphitic nanoparticles. Degree and nature of impurities vary with synthesis technique, Arc discharge having the most amount of catalyst Nanometal particles where in CVD the least impurities exist. These impurities may either lead total failure of device or enormous behaviour, depending upon quantum and nature of impurities. Removal of such undesirable material from as produced or pristine CNTs is called purification [1].

Similarly activation or surface functionalization of CNTs plays an essential role for improving dispersion and solubility of the nanotubes in various solutions to design new composite materials [15]. Functional groups graphitized on the tubes surfaces are found to be responsible for the various physico chemical and catalytic properties of the composite or hybrid material. The functional groups, containing oxygen can be introduced by mechanical or chemical routes [16]. It is known that the amount and type of oxygen containing functional groups depend on the treatment methods. Many researchers focus on how to modify it as well as to characterize the surface functional groups of carbon [17].

One of the objectives of this research project was to remove residual Nanometal particles, amorphous carbons and graphite Nanoparticles from as received/raw CNTs. Two different techniques were employed for the said purpose; one was used in order to eliminate the metal catalyst from CNTs and the other one for the removing of amorphous carbon in order to achieve more surface area of CNTs for further doping purpose. The removal of the metal catalyst was carried out by refluxing the CNTs in nitric acid and removing of amorphous carbons was done by air oxidation and heat treatment for few hours. Sonication was done as an initial step in order to disperse CNTs since these are insoluble in most solvents and get agglomerated. Impurities also get trapped inside the agglomeration making itself unavailable for acid digestion. So dispersion of CNTs in a suitable medium is necessary for dissolution and separation of these impurities [1]. Detail of the same experimental work will be discussed in the subsequent chapter.

1.2.4. Synthesis Technique of Nanocomposite

The synthesis of Fe-CNTscomposite is both of technological and fundamental interest as the nanocomposite material exhibits unique properties of CNTs and Iron/Iron Oxide Nanoparticles. Similarly a new species of nanocomposites can be synthesised by incorporating various metal/metal oxide in the same very way thus a composite can be fabricated with extra ordinary characteristics, meeting a wide range of applications in different disciplines. For example, Alumina has good oxidation resistance and high hardness is used widely as a ceramic material but it has limited applications due to its low fracture toughness. Thus CNTs can be used to reinforce its alumina fracture toughness, owing to CNTs unique 1-D structure with robust thermal and mechanical properties [18]. Here CNTs are used as sorbents.

Different techniques are used to synthesize CNTs/Metal Oxides composites. This includes Pressures Sintering, Hot Pressing of Composite Powder, Spontaneous Formation of Metal Oxide Nanoparticles on CNTs, In Situ CVD Synthesis Route, Decomposition of metal oxides precursor directly onto the surface of carbon nanotube etc. However, the Wet Chemistry technique is the most widely utilized method. One of the most important reasons of its popularity is cost comparing and simplicity to others techniques. However, in this method, functionalization or activation of CNTs is a primary step that must be taken before the synthesis of CNTs/Metal Oxides nanocomposite material. Activation or functionalization of CNTs plays an important role in facilitating the binding, embedding or loading of Nanoparticles on the surface of nanotubes since it introduces chemical functional groups to the surface of nanotubes. The successful functionalization of the nanotubes is the first step to properly synthesise the nanocomposite materials from CNTs and metals [19].

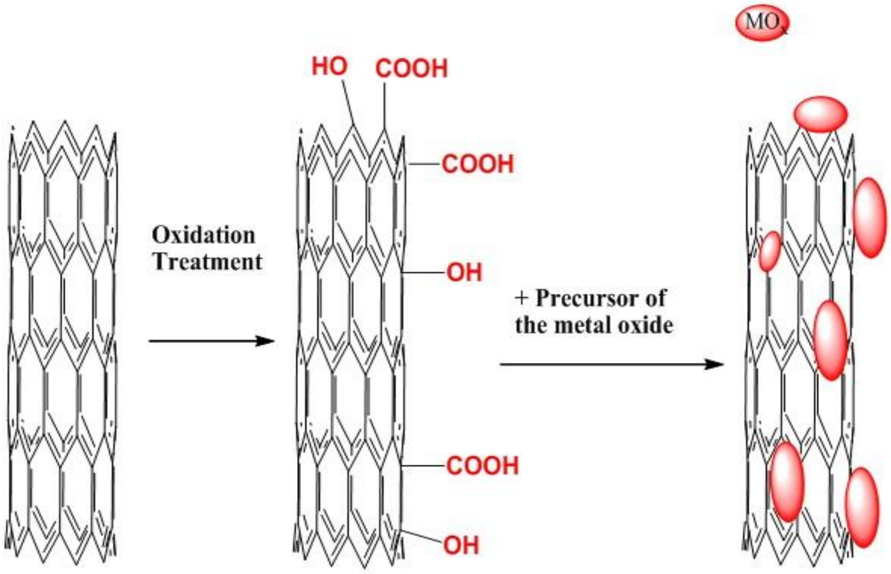


Figure 1.5: Structure of doped CNTs.

Chapter 2: Literature Study

2. *In this chapter, scientific work so far done on photo ignition of CNTs, their doping with different metals/metal oxides, characterization and various applications as nanocomposite and Nano energetic material is reported. literature survey and review, on the subject matter is presented systematically.*

2.1. Photo Ignition of CNTs

In June 2005, M. R. Manaa et al. loaded 0.020 g of loosely packed SWCNTs on top of 30 g of K-6 explosive, 2- Oxo- 1,3,5 trinitro triaza cyclohexene ($C_3H_4N_6O_7$). A flash bulb was installed 5 cm above the funnel containing SWCNTs and K-6. Flashing resulted in initial deflagration of K-6 for approximately 1.5 minutes followed by a detonation. A shock wave with an average speed of 6.6 km/second was observed. On the product of ignition fluffy SWCNTs it was found that flashed Nanoparticles were mainly consist of fused Fe_2O_3. It was concluded that higher the content of Nanometal catalyst particles, easier the ignition of CNTs. Moreover it was also observed that by ignition of SWCNTs through photo flashing, rise in local temp was estimated to be in the range of 1500 ^{o}C to 2000 ^{o}C [14].

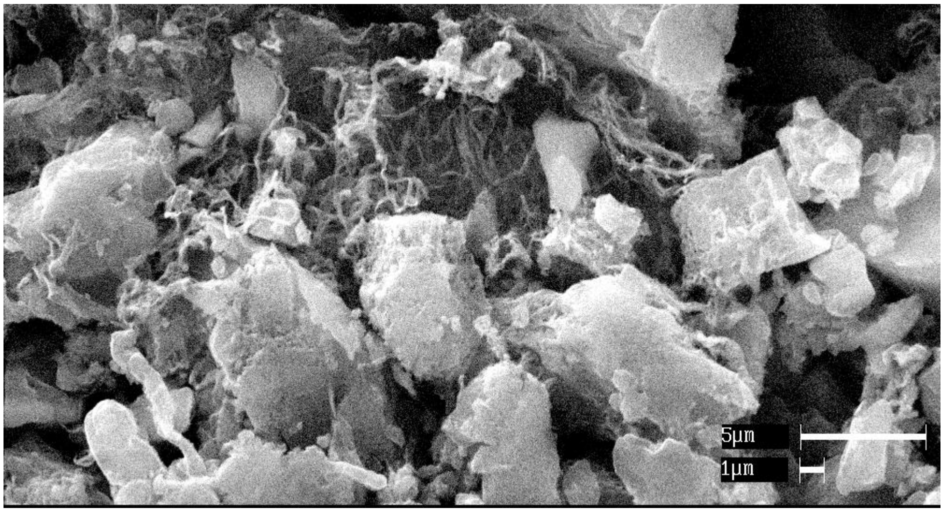


Figure 2.1: SEM Image showing micron size PETN grains among SWCNTs.

In July 2007, Shih H. Tseng et al. demonstrated that ignition in CNTs was due to agitated oxidation of Nano iron particles, exposed in air upon camera flashing. Fluffy SWCNTs, fluffy MWCNTs, compacted SWCNTs, Carbon fibers, Carbon Powder and purified SWCNTs were subjected to light flashing and integrated intensities of acoustic wave found in the same order i.e. maximum for fluffy SWCNTs. TGA analysis was done and it was found that the content of catalyst nanoparticles to trigger SWCNTs must be between 13.8% to 30%. Low intensity of photo acoustic effect without ignition was detected when purified SWCNTs were subjected to light flashing. Experimental results indicated that temperature increase exceeded 475 ^{o}C in SWCNTs and MWCNTs by mixing Ferrocene with CNTs [12].

2.2. Purification and Functionalization of CNTs

In June 2011, M. Stancu et al. applied two approaches to purify the pristine/ raw MWCNTS. In first approach wet oxidation of MWCNTs was done by refluxing in strong acids i.e. HNO_3 and HCl separately for 6 hours and then to remove amorphous carbon, oxidation of CNTs was done in air by heating it at 550 ^{o}C for 10 minutes. Analysis and characterization of CNTs were done by using FE-SEM, TEM, XRD, Raman spectra. It was observed that oxidation of CNTs in air removed amorphous carbon but D- band was not eliminated. However highly purified CNTs were achieved [20].

In July 2007, Maxim N. Tchoul et al. conducted oxidation of SWCNTs by refluxing HNO_3. CNTS were first sonicated in order to get its dispersion in nitric acid and then reflux was done. By doing so CNTs were functionalization as well as amorphous carbons and residual nanometal catalyst particles were removed. Thus purification and activation by wet oxidation of CNTs were achieved. It was observed that more intensive oxidation i.e. by increasing the oxidation time caused more functional groups to attach on the surface of CNTs but more defects and shortening of tubes length also occurred. It was found that solubility of CNTs in polar solvent also increased with activation of CNTs by functionalization. Raman spectroscopy, FTIR and AFM were used to characterized the activated CNTs [21].

2.3. Thermal Decomposition of CNTs

In May 2012 Amit Mahajan et al. investigated the thermal behaviour of MWCNTs under different environments. And decomposition of CNTs was studied. It was observed that under air environment CNTs started decomposing at about 420 ^{o}C but changes in morphology was observed at about 400 ^{o}C. Similarly it was observed that CNTs were oxidized at 200 ^{o}C in oxygen rich environment. However CNTs remained un-decomposed up to 1300 ^{o}C in argon environment. It was noticed that in air activation energy of MWCNTs was calculated between 80 and 108 kJ/mol. TG/DTA, XRD and Raman spectroscopy were used as basic analytical techniques [22].

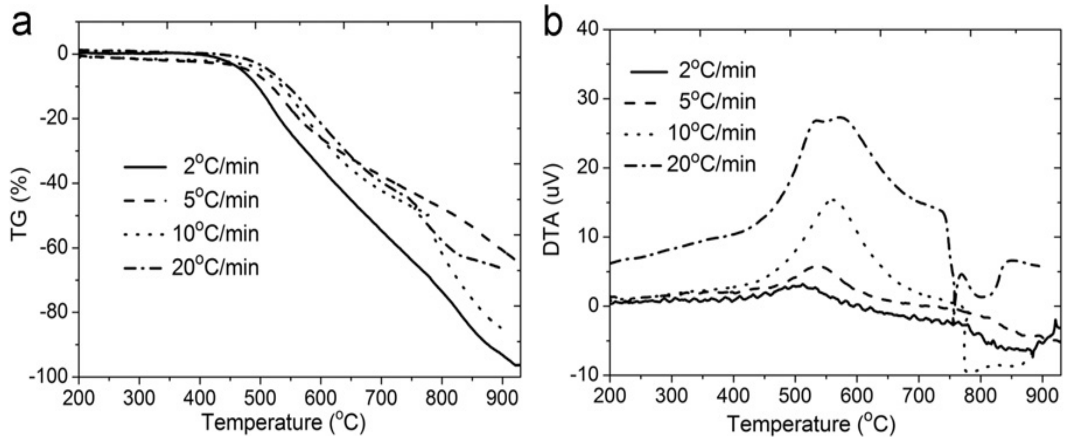
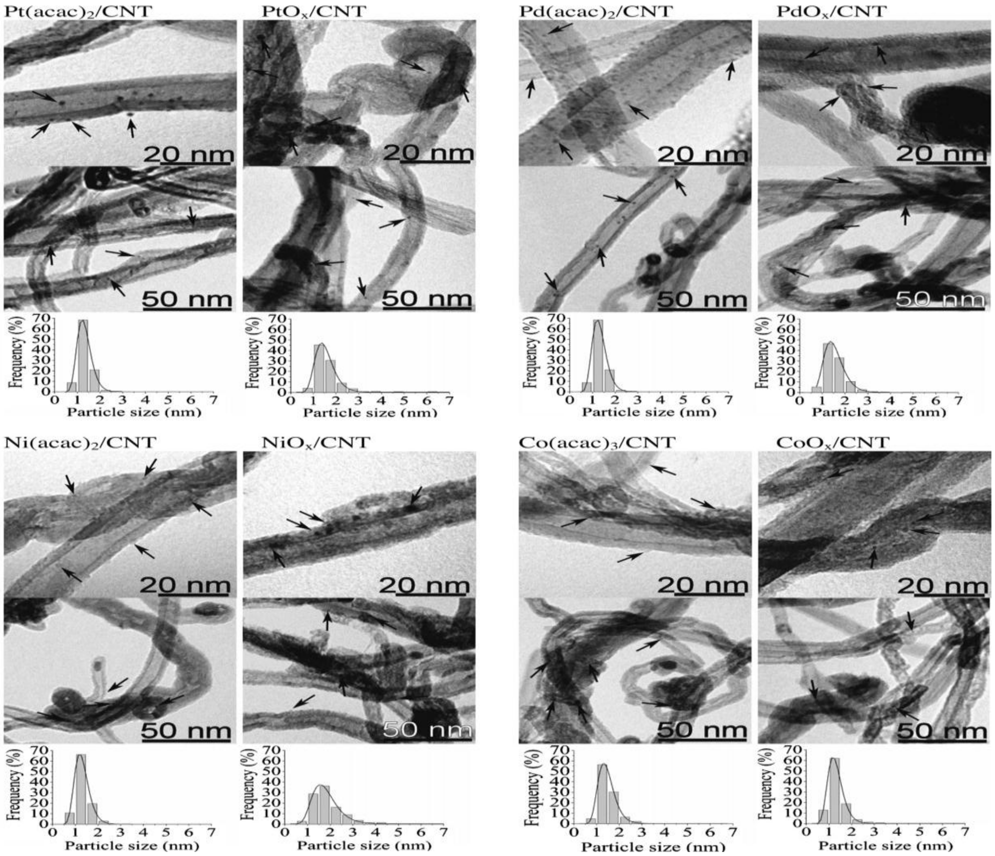


Figure 2.2: TG (a) and DTA (b) of MWCNTs conducted at different heating rates.

2.4. Low Temperature Oxidation of MWCNTs

In June 2009, Blazej Scheibe et al. presented their work in which they worked on the synthesis of MWCNTs by CVD method, its oxidation and subsequent reduction. The CNTs were sonicated in HCl in order to purify these tubes from amorphous carbon and catalyst particles. The same CNTs were refluxed in strong acid for its oxidation. Then the oxidized CNTs were reduced by adding sodium borohydride powder (w/w = 5:1 $NaBH_4$ / MWCNTs). The reduced CNTs were dried under vacuum to degas adsorbed CO_2 and H_2O. FTIR was used to analyzed the surface of pristine, oxidized and reduced CNTs. TG/DTA was used for thermal characterization of samples and it was observed that the initial ignition temperature of the pristine, oxidized and reduced MWCNTs were 350 ^{o}C, 300 ^{o}C and 250 ^{o}C respectively [23].

In September 2012, Anne Riikka Leino et al. reported in his work, titled as "low temperature catalytic oxidation of MWCNTS" a significant decrease in ignition of CNTs from 500 ^{o}C to 200 ^{o}C by impregnation of Nanometal particles i.e. Pt, Pd, Ni and Co. In this work MWCNTs were first purified and then dispersed in toluene by ultra sonic agitation and then metal acetyl acetonate as a metal precursor was added in the final product, which was 2% metal by wt.. The solvent was evaporated and the product was annealed at different temperatures. Surprisingly, it was observed that defects produced by partial oxidation of the CNTs did not in practice have any influence on the enhancement of its further oxidation. TEM, EDS, XPS and TGA were used to analyse the samples [24].



$Pt(acac)_2/CNT$ PtO_x/CNT $Pd(acac)_2/CNT$ PdO_x/CNT

$Ni(acac)_2/CNT$ NiO_x/CNT $Co(acac)_3/CNT$ CoO_x/CNT

Figure 2.3: TEM images and PSA of metals precursors and oxide decorated CNTs.

2.5. Fabrication of CNTs/Metal Oxides Composite

In July 2011, Vinod K. Gupta and Tawfik A. Saleh published their work in shape of a chapter in the book, titled as "Carbon nanotubes – From Research to Application." In this work the synthesis strategy of a nanocomposite material consisting of CNTs and Metal Oxides was elaborated. Functionalization or activation of CNTs is also reported by oxidation treatment. The oxidized CNTs were dispersed in a solvent like ethanol or acetone etc. Similarly metal precursor was also dissolved in the same solvent and dispersion was achieved by sonication. After reflux and washing the material was calcinated to achieve the final product i.e. CNTs coated with metal and metal oxide. Different analytical techniques were used e.g. FTIR, XRD, SEM, TG/DTA and EDS. These nanocomposites were used as sorbents and catalysts [18].

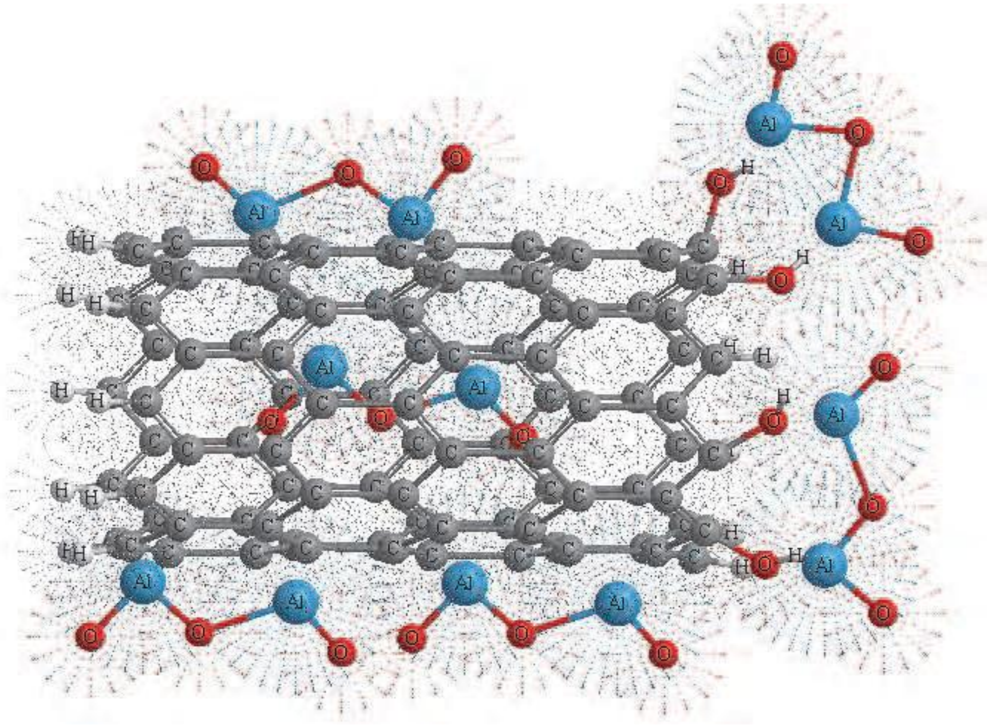


Figure 2.4: Structural representation of interaction between Al_2O_3 and CNTs.

In March 2012, Fan Zhao et al. investigated the synthesis and characterization of CNTs/ Fe composite. By using different concentration of Fe on the surface of CNTs by facile solvo thermal method a composite material was fabricated. The magnetic properties and structure of the hybrid CNTs were analysed by using XRD, TEM, FTIR, PPMS and FE-SEM. In this process first of all CNTs were oxidized by wet oxidation and functional groups i.e. OH and COOH were attached on the surface of CNTs. Here ferrocene was used as iron precursor, which was dissolved in benzene and CNTs were dispersed by sonication. Then autoclave was used for further heat treatment at 500 ^{o}C for 12 hours. It was observed that CNTs-Fe composite was more efficient under 2:1 ratio of ferrocene to CNTs, due to the Fe nanoparticles were well distributed on the surfaces of nanotubes [19].

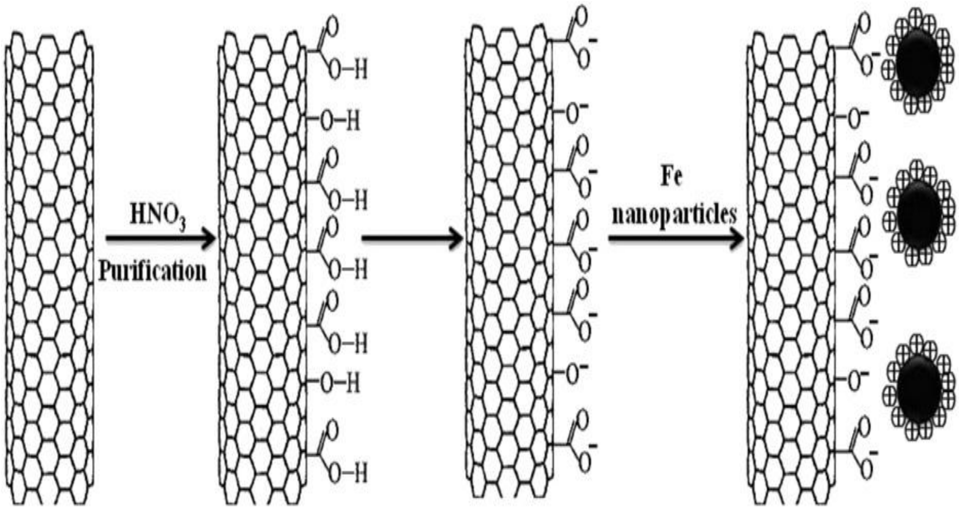


Figure 2.5: Fabrication process of CNTs-Fe composite.

2.6. Synthesis of Energetic Material

In March 2010, Christopher D. Malec et al. reported in their work; a mixture of MWCNTs and ferrocene prepared and was further doped with sodium perchlorate. Hence a combustible composite material was achieved, which was easily ignited by a camera flash. However a violent combustion was obtained when the same material was loaded on to the surface of porous Silicon film. Maximum brightness and energy was achieved when 5 mg mixture was doped with 20 mg of $NaClO_4$. It was observed that efficiency of the explosion was greatly dependent on the amount of oxidant. Excess oxidant abserved the energy released by combustion where as insufficient oxidant caused incomplete burning of the mixture. TGA and EDX were used for determining residual catalyst (Ni) Nanometal particles and SEM for morphology of Psi film. In this work it was proven that Nano structured energetic material might be fabricated by combining of MWCNTS with porous Silicon film, loaded with an oxidant and CNTs as photosensitive initiator [13].

Figure 2.6: Explosion of CNTs-Ferrocene loaded on pSi and doped with an oxidant.

In August 2013, Luke M. Currano et al. produced a Micro energetic material. In their patent work **M**WCNTs were synthesised by CVD technique, then a mixture of ferrocene and xylene vapours were exposed to a patterned SiO/Si substrate in a quartz tube furnace. The embodiment of solid oxidized was also done and the material was prone to initiate by electronic and optical means. TGA and DSC were used for determining thermal stability and heat flow of CNTs-$NaClO_4$ sample. SEM, XRD, FTIR, and X-Ray photo electron spectroscopy techniques were used to further analyse and characterize the final product. It was determined that **t**he micro explosive material could afford for a low or high explosion and the explosive material could also be used as a heat, gas and a shock wave generator [25].

2.7. Review of Literature Survey

While reviewing the literature survey, done for this research work it is very found that first time in years 2005 and 2007 photo ignition properties of CNTs was investigated but practical ignition was possible only for SWCNTs due to their wide surfaces area, low density and more easy conducting material. However for last five years work on doping of CNTs with different metal and metal oxides are being done. Thus synthesis of a nanocomposite material by maintain integrity of original material as well achieving the required characteristics.

It is important to highlight that no work has yet been reported for the synthesis of a Nano composite material as Nano energetic material by doping of MWCNTs with Fe nanoparticles and its ignition through single or multiple flashes of a photo camera. However more emphasis has been given on fabrication of nanocomposite material. This gives us a lead to fabricate a composite material, which is required to be easily ignited or initiated by photo flashing, electronic means and a laser pulse. This Nano energetic material may be considered a source of high energy, heat and gas.

Chapter 3: Experimental Methodology

3. *This chapter deals with the methodology and approaches used for experimental work and also highlights the means and ways adopted for characterization of raw material and the final product. Each approach is amply covered in subsequent paragraphs.*

3.1. Photo Ignition Characteristics of CNTs

Before starting with purification and synthesis of a nanocomposite, it was necessary to probe out the photo ignition characteristics of available raw material. Since, in years 2005 and 2007 in two separate works, it was reported that SWCNTS could be photo ignited due to their low density and greater surface area, as compared to MWCNTs [14, 24]. For this purpose an experiment was run and three different types of CNTs were subjected to camera flashing and results were analysed.

3.1.1. Experimental Details

Three types of MWCNTs, each with different specifications i.e. length, inner diameter, outer diameter of tubes, density, surface area and elemental composition, were named for experimental purpose as CNTs **A** , CNTs **B** and CNTs **C**. However only elemental contents of each CNTs were focused, especially residual nanometal particles.

About 15 mg from each CNTs was spread carefully onto a para film (stretched over a petri dish). Camera flash of Panasonic PE 28S was brought in close proximity to the CNTs at about 1.5 cm. Initially CNTs were exposed to single flash and subsequently multiple flashes and results were recorded. It was ensured that CNTs did not get compacted or dispersed too much. It was observed that non of CNTs types got ignited by photo flashing but popping in each type was heard with different intensity.

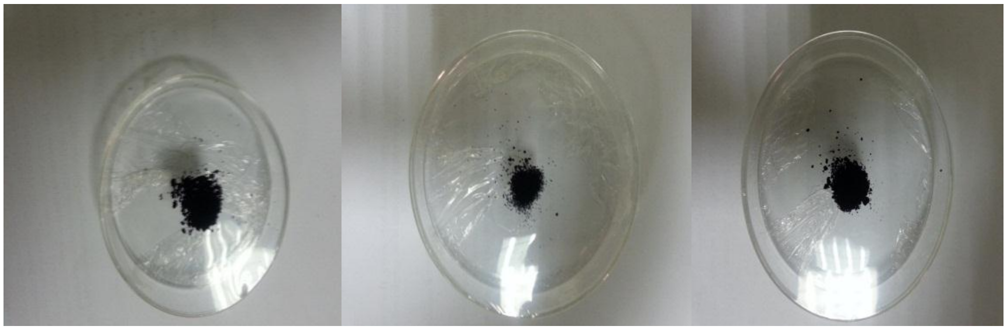


Figure 3.1: Post flashing of CNTs A (left), CNTs B (centre) and CNTs C (right).

In the second phase of this experimental work only CNT – **C** was selected in amount of about 25 mg and ferrocene of same quantity was added to it, thus making non homogenous mixture of CNTs-Ferrocene. The same mixture was put on a para film over 100 ml beaker and exposed to single light flash and then multiple flashes and it was noticed that mixture got ignited after few times flashings. However it was found that pure ferrocene could not get ignited by same photo flashes.

Figure 3.2: Images of ignited CNTs-Ferrocene mixture.

3.2. Purification and Activation of CNTs

The purpose was to remove residual Nanometal particles, amorphous carbons and graphite nanoparticles from received or raw CNTs. MWCNTs were purified applying two different techniques. One method was used in order to eliminate the metal catalyst from CNTs and the other one for the removing of amorphous carbon. The removal of the metal catalyst was carried out by refluxing the carbon nanotubes in nitric acid and removing of amorphous carbon was done by air oxidation and heat treatment for few hours. Prior to purification sonication was also done, in order to disperse CNTs as these are insoluble in most solvents and get agglomerated. Impurities also get trapped inside the agglomeration making itself unavailable for acid digestion. So dispersion of CNTs in a suitable medium is necessary for dissolution and separation of these impurities [1]. Moreover activation was also done by incorporating functional groups on CNTs surfaces. MWCNTs, with Purity: > 95 wt.%, Outside diameter: <7 nm, Inside diameter: 2-5 nm, Length: 10-30 um , SSA: > 500 m^2/g were selected as raw material for purification and activation. The process was carried out in four steps i.e. Sonication, Reflux, Centrifugation and Heat treatment. Chemicals and glassware used in the experiment are listed below:

Table 3.1: List of Chemicals and Glassware/Equipment Used.

Chemicals/Glassware	**Quantity/Size**	**Remarks**
MWCNTs	2 g	
HNO_3	200 ml	
Round Bottom Flask	500 ml	2 necks flask
Thermometer	1	Limit 400 ^oC
Centrifuge tubes	24	15 ml each

3.2.1. Sonication of Raw CNTs

2.2 g of CNTs were put in 500 ml round bottom flask and 200 ml of 70% concentrated nitric acid was also poured in the same flask with the help of a burette. The mixture was sonicated at 40 ^{o}C for 1 hour. It was considered that temperature did not rise above 45 ^{o}C at any instant. CNTs were sonicated in acid solution to open agglomeration of nanotube and anchoring acid solution uniformly on the tubes surfaces. After sonication a well dispersed CNTs in nitric acid were observed.

3.2.2. Reflux Process

The same sonicated mixture of CNTs-HNO_3 was refluxed for 4.5 hours at 123 ^{o}C in a oil bath. The flask was not filled over 2/3 full and apparatus was also examined for any leakage of vapours during reflux process. After completion the reflux process a dark brown solution was obtained and that was cooled down to room temperature. Reflux process made the solution became darker which showed that CNTs were much dispersed as compared to sonicated solution. At the end the homogenized solution got oxidized under reflux at 100 ^{o}C. Functional groups were introduced on to the CNTs surfaces.

Figure 3.3: Images of reflux process (left) and solution after reflux (right).

3.2.3. Centrifugation and Washing

The refluxed solution was poured into 23 x 15 ml centrifuge tubes, each tube contained 10 ml of solution and centrifugation was done for 20 minutes at 4000 RPM. A black sediment was found at the bottom of the tube and brownish supernatant was decanted off. The sediment was repeatedly suspended in de ionized water by vigorously shaking and followed by centrifugation for 6 minutes at 4000 RPM and decanting the supernatant. Such washing was done 4 times, with each washing cycle as the solution became less acidic, the supernatant solution became more darker. The sediment contained CNTs with a cover of a thick coating which was consist of acidic decomposition products i.e. carboxylated carbons (they were small polycyclic aromatic sheets, edge-terminated with carboxyl groups). These products were soluble in deionized water, which caused the solution black. The washed CNTs were shifted into a 500 ml beaker and kept these overnight for settlement of CNTs. Then the black CNTs paste was left and water was decanted off the beaker.

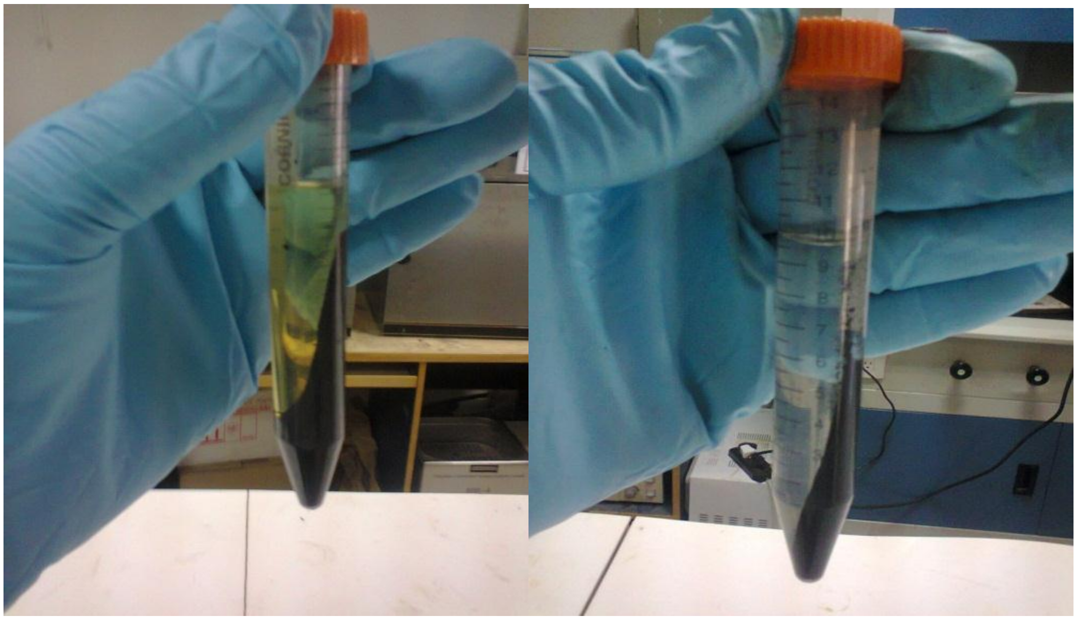


Figure 3.4: Images of CNTs after centrifuge and washing.

3.2.4. Heat Treatment

The final product was heated in air at 110 ^{o}C for 7 hours in order to remove moisture and dry the CNTs paste. Then the same solid CNTs was again heated at 350 ^{o}C for 2 hours to remove the amorphous carbon. After such heat treatment an agglomerated and crispy solid material was achieved. Then the same solid material was grinded in a mortar and pestle and fluffy powdered CNTs was achieved. Before grinding the mortar was cleaned with methanol to avoid addition of impurities in CNTs. However there was almost 400 mg wt. loss as purification was started with 2.2 g of raw CNTS and resultant purified CNTs were found of 1.85 g due to removal of amorphous carbon and residual meta nanoparticles.

Figure 3.5: Final product of CNTs after heat treatment.

3.3. Synthesis of a CNTs-Fe Nanocomposite

Synthesis of CNTs-Fe composite was of fundamental and technological value as the nanocomposite material exhibits the unique properties of CNTs and Nano Iron particles. In addition to that it also had some extraordinary properties caused by the interaction between them. Thus, a new type of nanocomposite was fabricated with extra ordinary properties meeting a wide range of applications in different disciplines [18].

By this work, an effective technique for the decoration of Fe nanoparticles on MWCNTs with various concentrations was formulated. Initial mass ratio of ferrocene to CNTs was manipulated in order to achieve the desired results. Thus by decorating CNTs with Fe nanoparticles lead us to the synthesis of nanocomposite material [19]. Chemicals and glassware were used in that experiment are listed below:

Table 3.2: List of Chemicals and Glassware Used in Experiment.

Chemicals/Glassware	Quantity/Size	Remarks
MWCNTs	100 mg	
Toluene	20 ml	
Ferrocene	In different ratios to CNTs	As a Fe precursor
Rotary Flask	100 ml	
Sodium perchlorate (mono hydrate)	In different ratios to CNTs	

3.3.1. Doping of CNTs with Fe Precursor

Purified and functionalized/activated CNTs were taken as a starting material and different wt. ratio of ferrocene as an iron precursor was dissolved in 20 ml toluene. CNTs were also dispersed by sonication in the same solution. For each sample (S) concentration of CNTs and toluene were kept constant and only concentration of ferrocene was increased as per required Fe wt. %. Since ferrocene contains 30% Fe by wt. therefore it was used as a source of Iron [26]. However Fe particles were found embedded on CNTs surfaces in very less concentration as compared to its existing percentage ratio in ferrocene. Following samples i.e. S1, S2, S3, S4, S5, S6, S7 and S8 were synthesised with different concentration ratio of Fe particles, impregnated on CNTs surfaces.

Table 3.3: Ingredient list of Each Sample.

Samples	CNTs	Ferrocene	Fe (wt)	Toluene
S1	100 mg	33 mg	10 %	20 ml
S2	100 mg	66 mg	20 %	20 ml
S3	100 mg	100 mg	30 %	20 ml
S4	100 mg	150 mg	45 %	20 ml
S5	100 mg	200 mg	60 %	20 ml
S6	100 mg	250 mg	75 %	20 ml
S7	100 mg	330 mg	100 %	20 ml
S8	100 mg	415 mg	125 %	20 ml

To obtain the final product, few steps consisting of soncation, evaporation of toluene, calcination, and light flashing of each sample was carried out. Each step is elaborated in the following paragraphs.

3.3.2. Sonication and Evaporation

The purified CNTs were sonicated ultrasonically at 50 ^{o}C and at frequency of 40 K Hz for 3 hours in order to achieve well dispersed CNTs in an homogenous solution of Ferrocene and toluene. Then the solvent (toluene) was evaporated at about 70 ^{o}C at 90 RPM by using Rotary vacuum. At the end of this process a product like black powder was collected from rotary flask.

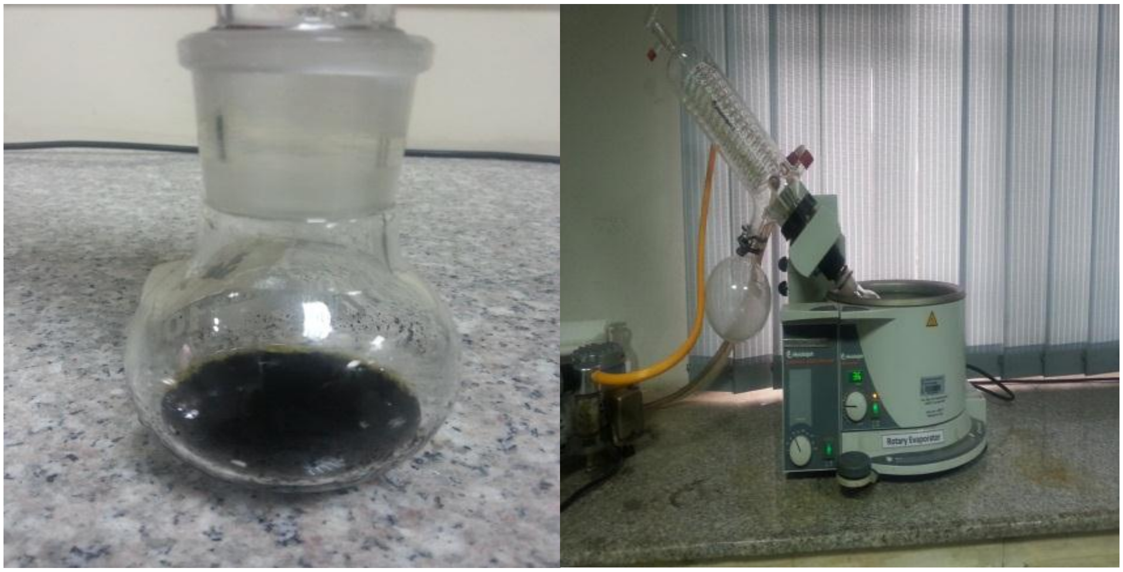


Figure 3.6: CNTs-Ferrocene after sonication (left) and rotary vacuum evaporation process (right).

Then three sub samples from each sample, named as **Sa**, **Sb** and **Sc** were heat treated (calcination) at different temperature and for different time period, in nitrogen, air and vacuum environment respectively. Heating rate was set to be 5 ^{o}C per minute to reach the required heating level. The post calcination doped CNTs was grinded to obtain final Nano material. Then these samples were placed in air tight glass vials for further analysis and application. It is important to highlight that best results were achieved by calcination in vacuum environment. Parameters set for calcination of samples are tabulated as under.

Table 3.4: List of Parameters Set for Calcination Process.

Heating Environment	Flow/Pressure	Temperature	Duration	Sub Samples
Nitrogen	15 psi	315 ^{o}C	1.5 hours	Sa
Air	Local	315 ^{o}C	1.5 hours	Sb
Vacuum	0.01 M Pa	200 ^{o}C	3 hours	Sc

3.3.3. Photo Flashing of Samples

About 15 mg of each sample S was put on para film (stretched over petri dish) and was exposed to camera light flashes for multiple times. It was observed that initial ignition occurred in sample with 15.89% Fe by wt. whereas maximum ignition efficiency was achieved from the sample with 32.22 % doped Nano Fe particles in the vacuum environment**.** Here result of photo flashing effect on 9 x samples with various concentrations of doped Fe particles is shown below.

Table 3.5: Photo Flashing Effect in Relation to Concentration of Doped Fe Nanoparticles.

Samples	Fe Doping	Nitrogen (Sa)	Air (Sb)	Vacuum (Sc)	Remarks
S6	75 % by wt	4 % by wt	11 % by wt	**16 % by wt**	Only samples **S6c**, **S7c** and **S8c** which were calcinated in **vacuum** got **ignited**
S7	100 % by wt	7 % by wt	14 % by wt	**18 % by wt**	
S8	125 % by wt	9 % by wt	19 % by wt	**32 % by wt**	

To prove that the ignition in Fe doped CNTs was due to the presence of Fe nanoparticles, A mixture of functionalized/activated CNTs and Ferrocene with 1:2 by wt. was also exposed to flash light and it was observed that CNTs/ Ferrocene mixture got ignited. However neither CNTs nor Ferrocene ignited when each material separately was exposed to photo flash. Photo flashing images of doped CNTs in the figure 3.7 below.

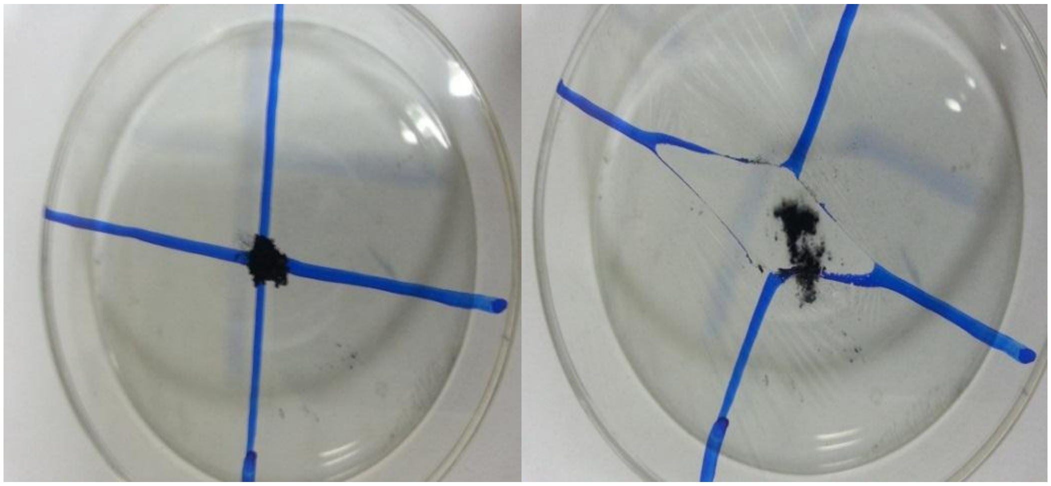


Figure 3.7: Pre flashing (left) and post flashing image (right) of Fe doped CNTs.

3.3.4. Intensity of Photo Flash

Intensity of camera photo flash used for ignition of Fe-CNTs was measured by light/lux metre. The meter was switched onto fluorescent mode and then taking multiples readings were taken and its aggregate was found as 13,972.7 lux. Following calculations were done.

100000 lux = 100 mW/cm^2 or 1000 W/m^2 or 1KW/m^2
13972.7 LUX = (100 mW/cm^2 X 100000) x 13972.7 lux
= 13.97 mW/cm^2 = 139.7 W/m^2
Flash duration = 10 ms = 10/1000 sec

Watts to joules calculation formula:

The energy *E* in joules (J) is equal to the power *P* in watts (W), times the time period *t* in seconds (s):

$$E_{(J)} = P_{(W)} \times t_{(s)}$$

$$J = W \times s$$

$$= 139.7\ \text{W/m}^2 \ \text{x}\ 10\ \text{ms}$$

$$= 139.7\ \text{W/m}^2 \ \text{x}\ 10/1000\ \text{s}$$

$$= 1.397\ \text{J/m}^2 = 1397\ \text{mJ/m}^2$$

3.3.5. Doping with Oxidant

Sodium perchlorate monohydrate ($NaClO_4.H_2O$) was used as an oxidant. Before mixing the oxidant with doped CNTs it was dehydrated by over night heating at 110 ^{o}C. Then it was mixed with sample, S8c (doped with 32% Fe concentration in vacuum environment). It was ensured that the mixture must neither be over oxidized nor under oxidized. This can only fit with 2:1 stoichiometry of the following reaction [13].

$$2C + NaClO_4 \longrightarrow NaCl + 2CO_2$$

Which implies that:-

$$\text{e.g.}\quad 24\ \text{g of C} \longrightarrow 122.4\ \text{g of } NaClO_4$$

$$1\ \text{g} \longrightarrow 122.4/24\ \text{g}$$

$$100\ \text{mg of C requires} \longrightarrow 122.4/24 \times 100\ \text{mg of } NaClO_4$$

$$510\ \text{mg of } NaClO_4$$

The end product called as nEM (Nano Energetic Material) was obtained and was subjected to photo flash initiating mechanisms.

3.4. Analytical Techniques

Various analytical techniques were used for characterization of raw, functionalized/activated and hybrid CNTs. The morphology and composition of these samples were analysed by FE-SEM and EDS. FTIR was used to analyse the functional groups and TG/DTA was employed to perform thermal analysis. XRD was used to investigate the quality and crystalline nature of nanotubes as opposed to amorphous carbon materials [19] and bomb calorimeter was employed to ascertain the enthalpy of combustion of nEM. Light/lux metre was used to ascertain the light intensity of Photo camera flash. Analytical results obtained, will be discussed in next chapter, however for understanding purpose, the functioning and working principles of these instruments are illustrated here briefly.

3.4.1. Field Emission Scanning Electron Microscope (FE-SEM)

FE-SEM is a sort of electron micro scope that generates images of a sample by scanning it with focused electrons and with improved spatial resolution and less damage to sample than conventional SEM. By interaction of electrons with atoms in the sample, various signals are produced and detected, which contain information about the sample's surface topography and composition. Samples can be observed in low vacuum, high vacuum, in wet conditions and at a wide range of elevated temperatures.

FE-SEM produces various signals and the three most important are; secondary electrons , back-scattered electrons, characteristic X-rays. It is very rear that for all possible signals there should be detectors. However in all FE-SEM or SEMs secondary electron detectors are standard. The signals produced by electron beam with atoms at the surface of the specimen produces high resolution image. Magnifications of image up to a wide range is possible i.e. from 10 times to more than 500,000 times.

Before starting with characterization of samples these are required to be prepared in order to achieve the better images therefore samples must be conductive electrically. Since the samples (CNTs) are conductive but due to modification or doping with Nanometal particles, the specimen was coated with gold. As the specimen was in fluffy powder form therefor it was stuck on a carbon adhesive tape which was further attached to a stub. Coating was done by low vacuum sputtering technique.

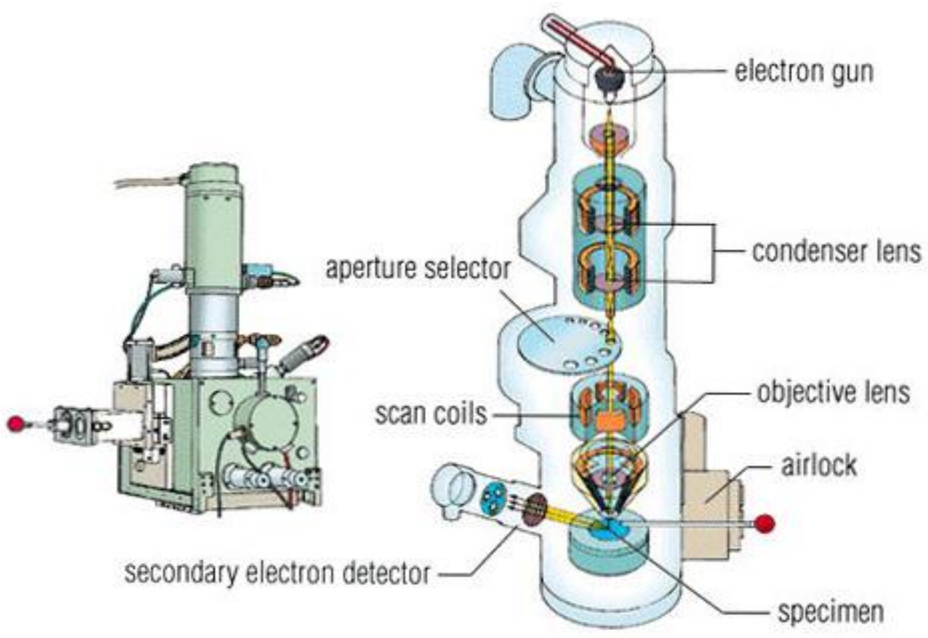


Figure 3.8: Schematic diagram of FE-SEM.

3.4.2. Energy Dispersive X-Ray Spectroscopy (EDS)

EDS is an analytical technique used to find out the elemental composition of a sample. It works on the fundamental principle that each element has a unique atomic configuration, which allows a unique set of peaks on its X-ray spectrum. It is mostly set with SEM so that high energy beam of electrons exciting the atom from ground state to excited state and an electron from an outer shell occupies the inner shell and release energy in the form of a X Ray. The energy, emitted is measured by an energy dispersive spectrometer. The same energy corresponds to the atomic structure of the element from which it is emitted. Thus elemental composition of a sample, under analysis is measured. In this case EDS was already attached with SEM system and no sample preparation or additional arrangement was made for analysis purpose. Elemental composition of raw CNTs, functionalized CNTs and final product was determined.

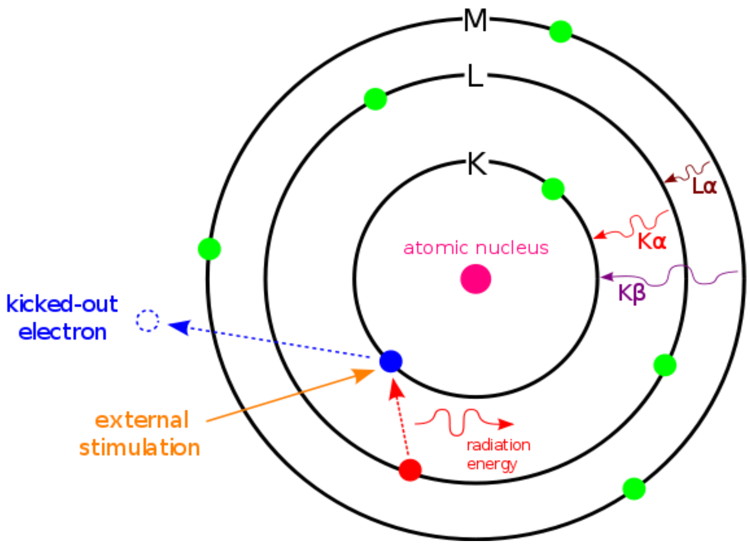


Figure 3.9: Schematic diagram showing working principle of EDS.

3.4.3. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a technique used to obtain an infrared spectrum of absorption, emission, photo conductivity of a solid, liquid or gas sample. The aim in this technique is to know that how much a specimen absorbs light at each wave length. Then computer programme is required to convert the raw data for each wavelength into light absorption measurements. Mostly FTIR technique is used to find out the functional groups.

We had CNTs powder as sample in nanosize, therefore KBr pellets were used. First of all KBr powder, being hygroscopic, was dried in oven at 110 ^{o}C for 1 hour, to remove moisture. Then few mg of sample was mixed in KBr and a pellets were made out of it by compressing it under pressure. In order to make sure that our samples might not get contaminated, the stainless steel disks, used for making of pellets were thoroughly cleaned with ethanol.

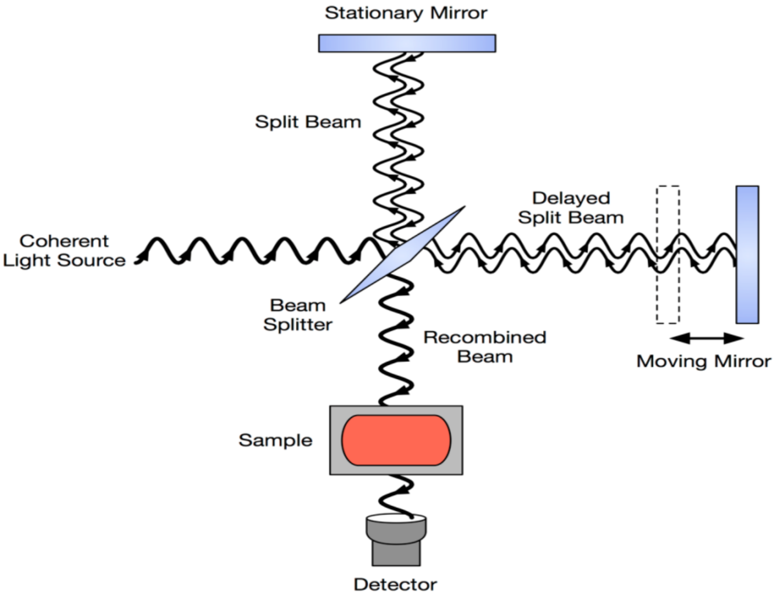


Figure 3.10: Schematic diagram of FTIR.

3.4.4. Thermogravimetry and Differential Thermal Analyser (TG/DTA)

TGA is a technique, used for thermal analysis of a specimen, in which changes in chemical and physical properties of materials are determined. It is commonly used to ascertain specific characteristics of a sample that exhibits either mass loss or gain due to oxidation, decomposition or loss of volatiles such as moisture. DTA is a technique, in which changes in a sample under analysis are determined in shape of either as endothermic or exothermic peak. Enthalpy change is represented by area under the peak.

To start with TG/DTA analysis about 3.5 mg of sample was loaded in the alumina pan and was placed inside the furnace. Temperature range was set from 25 ^{o}C to 900 ^{o}C at the rate of 10 ^{o}C per minute. Sample was analysed in air environment and flow rate was kept at 100 ml/minute or 100 SCCM.

3.4.5. X–Ray Diffraction (XRD)

XRD is non destructive technique, used for analysis of all kind of material including solids, fluids, powder and crystals. Generally, this technique is used to analyse the crystalline structure of a material. It is used to determine the unit cell parameters of a crystalline, by interaction of X Rays with material at different angles on different planes. Thus different peaks are generated, which tell us the location of peaks by applying Bragg’s law with the help of Miller indices. These indices are related to inter planer spaces. Scherer’s is used to find out the crystalline size but crystallite size must be less than 100 nm. The intensity of peak shows the purity and concentration of a compound/element.

No special arrangement was required for preparation of sample, however in existing system the radiation source was Cu K-Alpha. Our samples were mostly consist of CNTs powder and about 20 mg of the same were loaded in crucible.

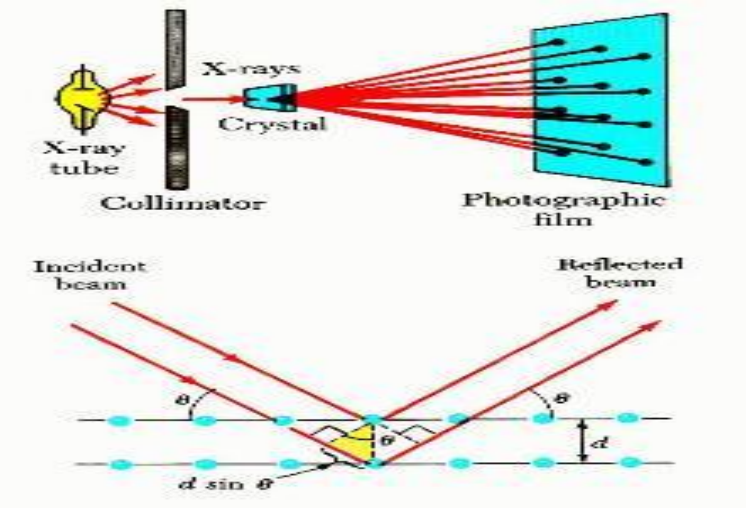


Figure 3.11: Working principle of XRD.

3.4.6. Bomb Calorimeter

Bomb calorimeter is used to find the heat of combustion or enthalpy of a chemical or physical reaction. It is a sort of constant volume calorimeter. Electric mean is used to ignite the specimen by burning of sample. Surrounding air gets heat up and escape through a copper tube which also heats up the tube and subsequently temperature of water, surrounding the tube also risen up. The change in water temperature leads to ascertain the calories content of the specimen.

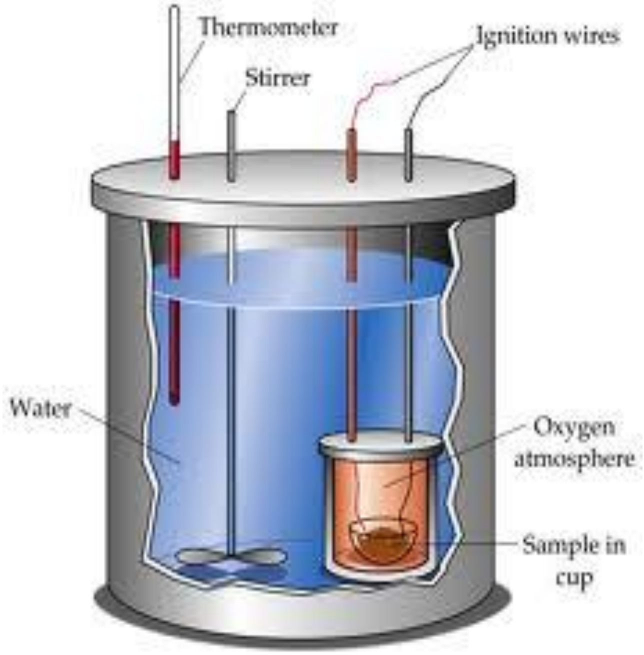


Figure 3.12: Schematic diagram of Bomb Calorimeter.

Chapter 4: Results and Discussion

4. *In this chapter, analysis of data, obtained through various analytical techniques and results achieved by modification in raw material is discussed and presented in a logical manner. Moreover photo flashing characteristics of raw CNTs, analysis of purified/activated CNTs, final results achieved through doping and important findings are covered here in detail.*

4.1. Photo Flashing Effects on CNTs

Photo flashing effects on CNTs ignition in relation to metal nanoparticles content plays an important role. To probe out the same relationship an experiment was carried out as mentioned in section 3.1, chapter 3 of this research study. Where three types of CNTs as CNTs **A** , CNTs **B** and CNTs **C** were tested. Analytical results and findings of the experiment are elaborated as under.

4.1.1. Analysis of Data – Photo Flashing Effects

When all three CNTs samples were subjected to single photo flash, no ignition of CNTs was observed even after multiple flashes i.e. up to 30 times. However audible popping was noticed. CNTs – **C** with minimum metal content was mixed with ferrocene (source of iron) then its ignition and popping sound on single flash were found. When the same sample was subjected to multiple flashes the sample got decomposed increasingly. It was also noticed that since mixture of CNTs and ferrocene was not in complete homogeneous form therefore some quantity of ferrocene was left un burnt, which was visible in yellow powder form. EDS spectrum is tabulated on the next page to shown the elemental composition of these CNTs.

Table 4.1: EDS Comparison of CNTs Samples.

Elements	**CNTs A**		**CNTs B**		**CNTs C**	
	wt.%	**Atomic%**	**wt.%**	**Atomic%**	**wt.%**	**Atomic%**
C K	92.44	95.20	95.10	97.71	92.81	94.90
O K	5.38	4.16	1.75	1.35	6.45	4.95
Al K	0.46	0.21	1.02	0.47	-	-
Cl K	0.34	0.12	-	-	-	-
Fe K	1.38	0.31	2.14	0.47	-	-
Ni K	-	-	-	-	0.75	0.16
Total	**100.00**		**100.00**		**100.00**	

4.1.2. FE-SEM Images and EDS Spectrum

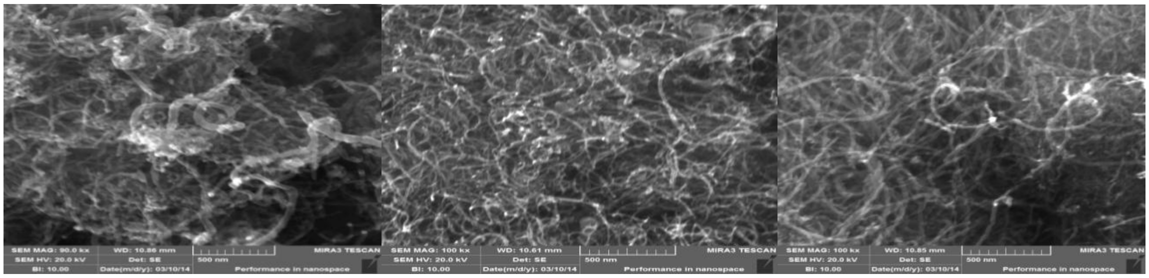


Figure 4.1: FE-SEM images of CNTs A (left), CNTs B (centre) and CNTs C (right).

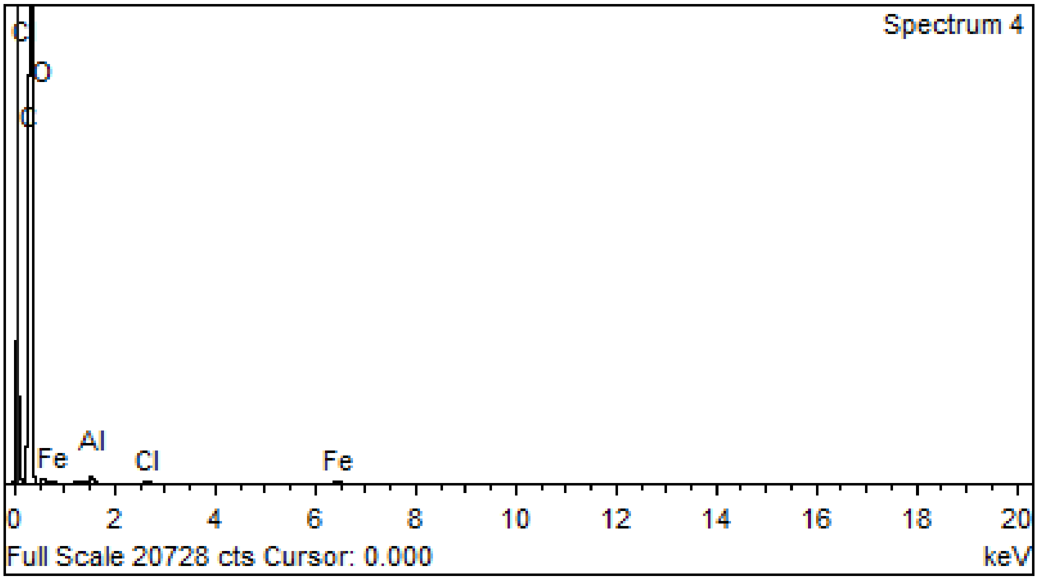


Figure 4.2: EDS spectrum of CNTs A.

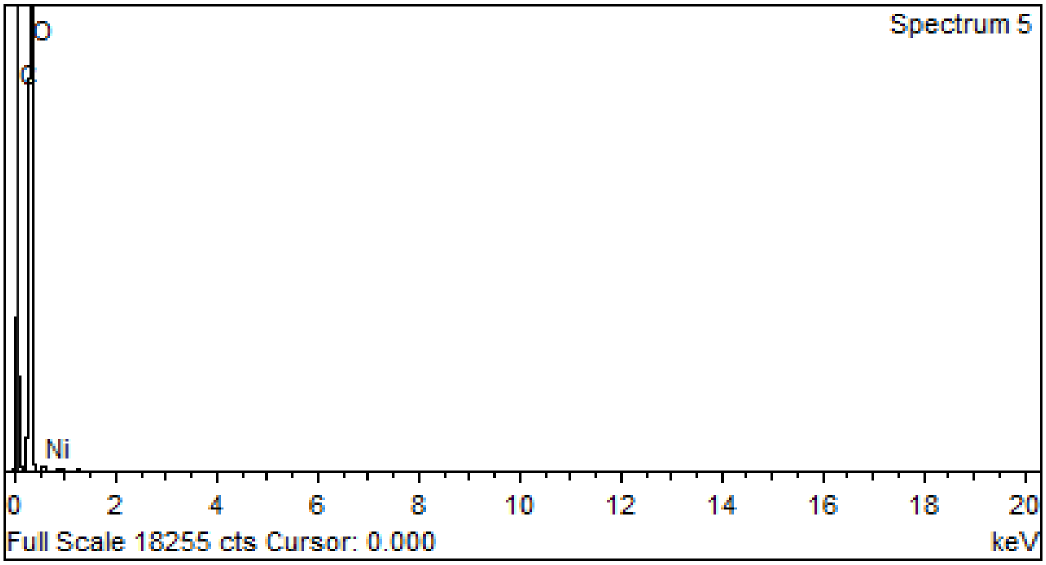


Figure 4.3: EDS spectrum of CNTs B.

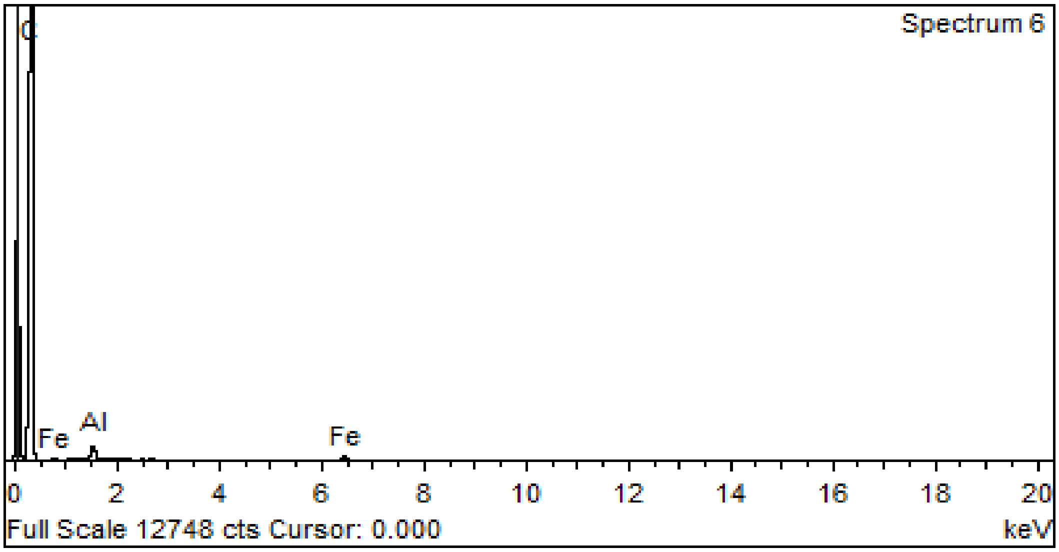


Figure 4.4: EDS spectrum of CNTs C.

4.1.3. Findings – Photo Flashing Effects

It is obvious from EDS results that CNTs – **B** had greater content of metal residual nanoparticles of Al and Fe in comparison to CNTs – **A**, where as CNTs – **C** had only Ni in very minute concentration, however none of CNTs could ignite. On the other hand CNTs and ferrocene mixture ignited as Fe nanoparticles were released from the same ferrocene compound and further oxidised in air which produced sufficient energy to ignite the CNTs. Ignition temperature of pure CNTs was about 750 ^{o}C and ferrocene had 480 ^{o}C but due to 1-D in nature, the heat accumulation in CNTs was faster than heat dissipation. Important findings are elaborated as following.

- The nanoparticles in sufficient concentration, contained by CNTs played a key role in its ignition by exposing to bright but short duration photo flash.
- The popping sound was due to photo acoustic response of CNTs, which was basically because of air expansion i.e. a vibration effect generated by light energy. Maximum popping sound was heard in the order of CNTs – **B** > CNTs – **A** > CNTs – **C**. This showed that more nanometal content caused greater acoustic effects in CNTs.
- It is also important to highlight that all three CNTs were in raw condition, which had some quantity of amorphous carbon as well as graphitic nanoparticles. It was

must to purify the raw or as received CNTs in order to make these tubes more prone to ignition by photo flashing.

4.2. Purification and Activation of CNTs

The second phase of experimental work was to purify the raw CNTs from residual nanometal particles and amorphous carbons and also to activate the same by attaching functional groups on their surface. So as explained in section 3.2 of chapter 3, the detailed procedure was followed.

4.2.1. Analysis of Data – Purification Process

In order to analysis the level of purification of CNTs, raw as well purified and activated samples were characterized by using EDS, FE-SEM, FTIR and TG/DTA techniques.

4.2.1.1. EDS Spectrum

EDS measurements were used for quantitative representation of the elemental components. Which showed that Ni metal content reduced drastically by purification from 3.00% by wt. to 0.64% wt. and O content increased in purified CNTs up to 5.23% wt. as compared to raw CNTs due to wet oxidation process for purification and activation as a result of grafting oxygen containing functional groups. Tabulated data is provided on next page.

Table 4.2: EDS Spectrum of Raw CNTs and Purified/Activated CNTs.

Elements	**Raw CNTs**		**Purified/Activated CNTs**	
	wt.%	**Atomic%**	**wt.%**	**Atomic%**
C K	97.00	99.37	94.13	95.87
O K	-	-	5.23	4.00
Ni K	3.00	0.63	0.64	0.13
Total	**100.00**		**100.00**	

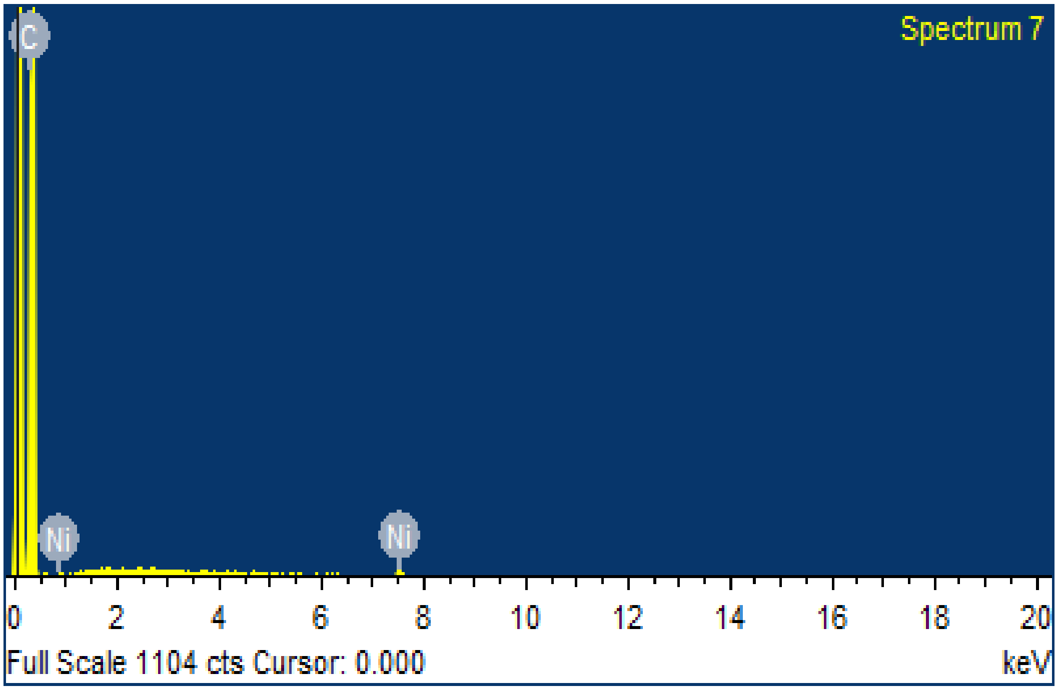


Figure 4.5: EDS spectrum of raw CNTs.

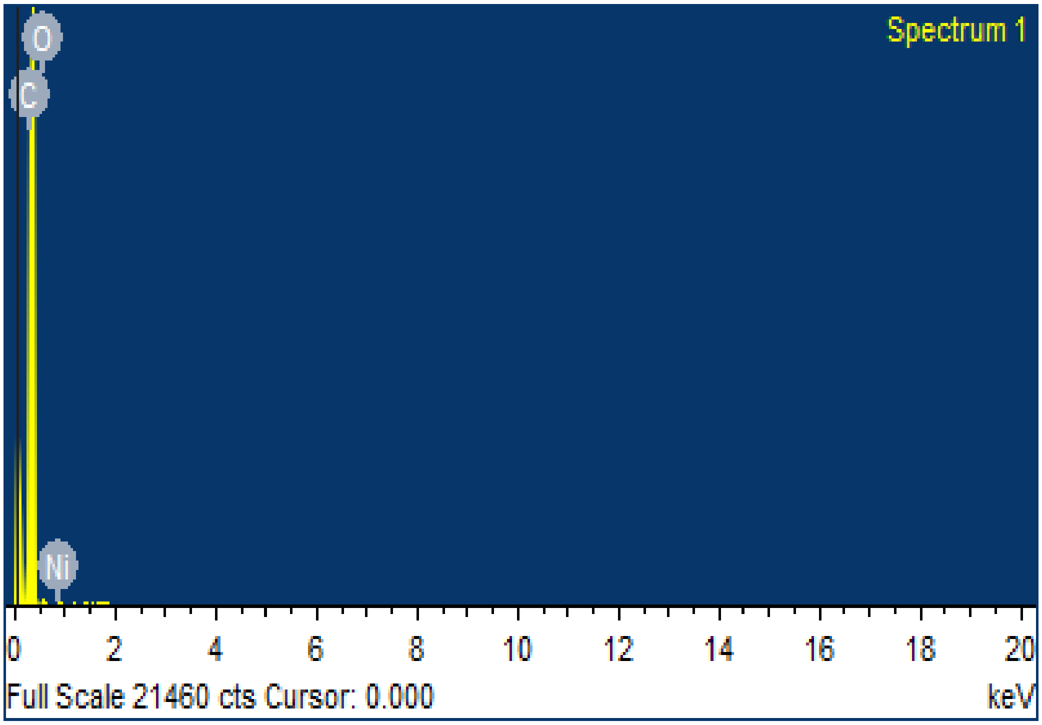


Figure 4.6: EDS spectrum of purified/activated CNTs.

4.2.1.2. FE-SEM Results

FE-SEM images at very high magnification showed black dots on the body of pre treated CNTs as impurities, such as amorphous carbons and nanometal particles. However, damage to the surface of CNTs by chemical treatment could also be observed. But here the purified CNTs showed no distortion or defects in CNTs by acid treatment at least at the level of FE-SEM images. Moreover CNTs after purification and activated with functional groups could be seen well dispersed and with very low in impurities. FE-SEM images at 500 nm range are shown here. Difference in structure and morphology of raw and purified/activated CNTs can easily be noticed.

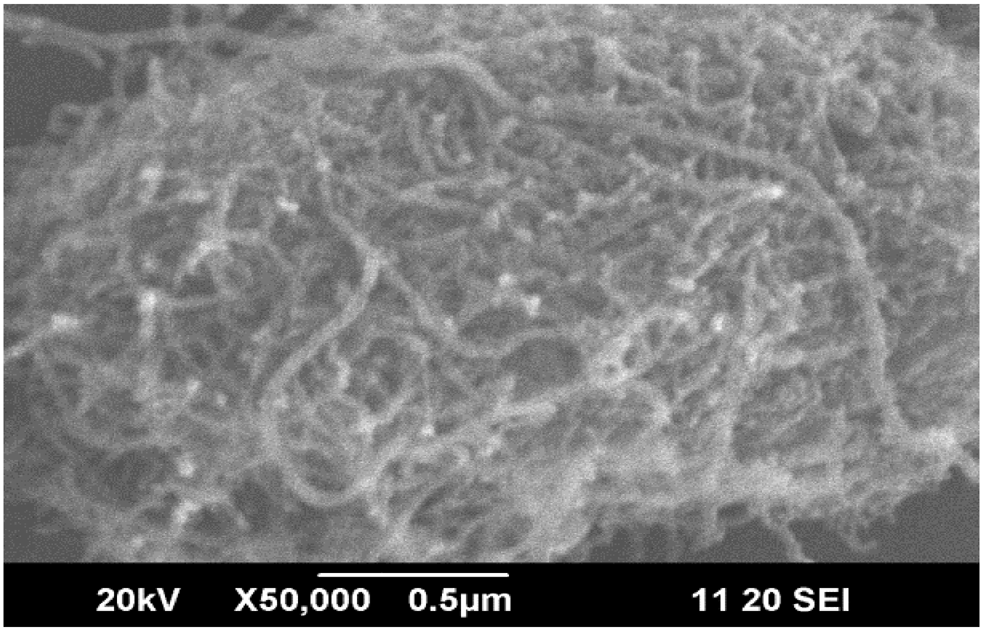


Figure 4.7: FE-SEM images of raw CNTs.

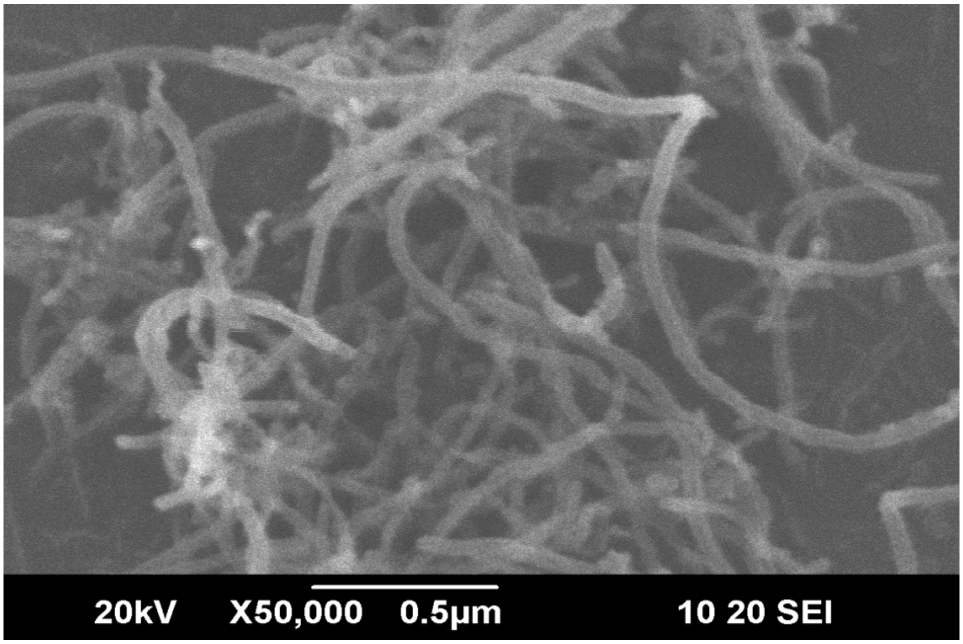


Figure 4.8: FE-SEM images of purified and activated CNTs C.

4.2.1.3. FTIR Results

The FTIR spectrum of functionalized/activated CNTs was used to analyse the functional groups i.e. hydroxyl (OH) and carboxyl (COOH) groups, attached to CNTs and also various characteristics bands were ascertained. Below figures show FTIR spectra from 400 to 4000 cm^{-1} of functionalized/activated as well as raw CNTs. It was found that a strong peak at 3422 cm^{-1} indicated hydroxyl groups and peak at 1636 cm^{-1} showsed carbonyl of carboxyl groups on functionalized CNTs surface. The weak Peak at 2920 cm^{-1} showed methylene group (C -H) from a long alkyl chain and the peak at 1429 cm^{-1} was associated with C = C vibration attributed to carbon skeleton. However in the raw CNTs spectrum there was a relatively weak peak at 3422 cm^{-1} corresponding to hydroxyl group due to moisture and peak at 1629 cm^{-1} showed some residue used in the perpetration of CNTs, which was not available in the spectrum of purified CNTs, hence removed during purification and functionalization process.

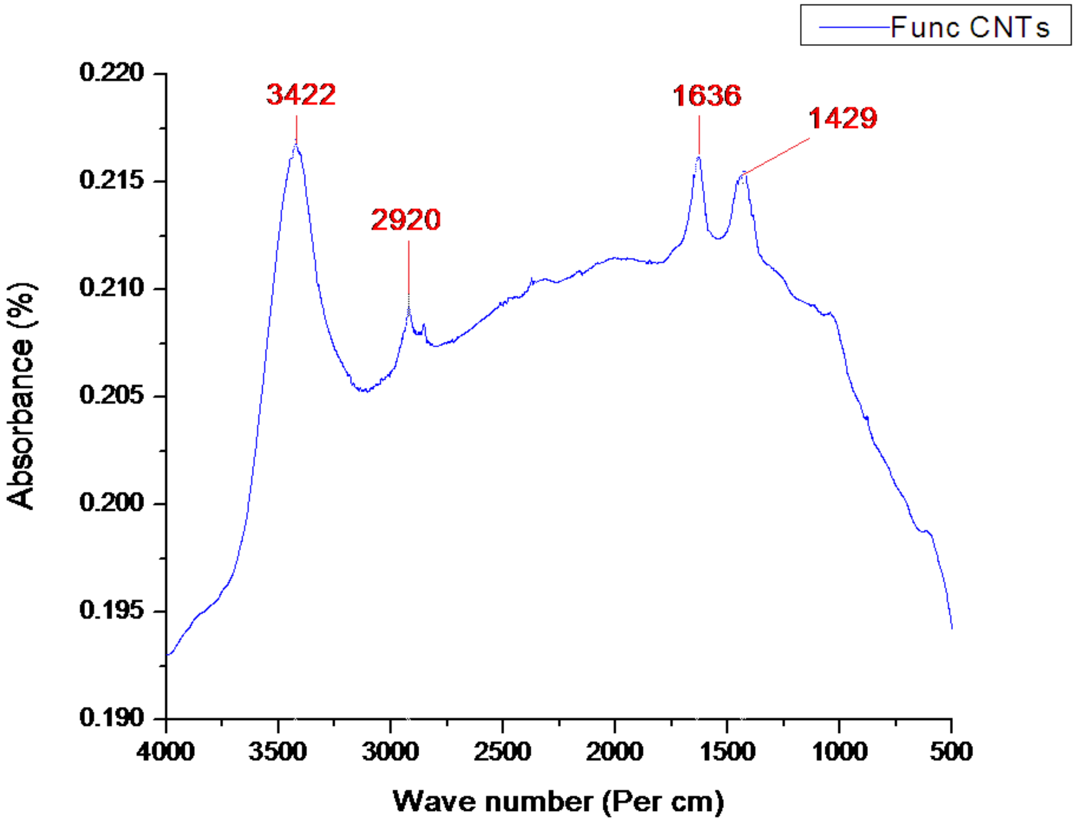


Figure 4.9: FTIR spectrum of purified/activated CNTs.

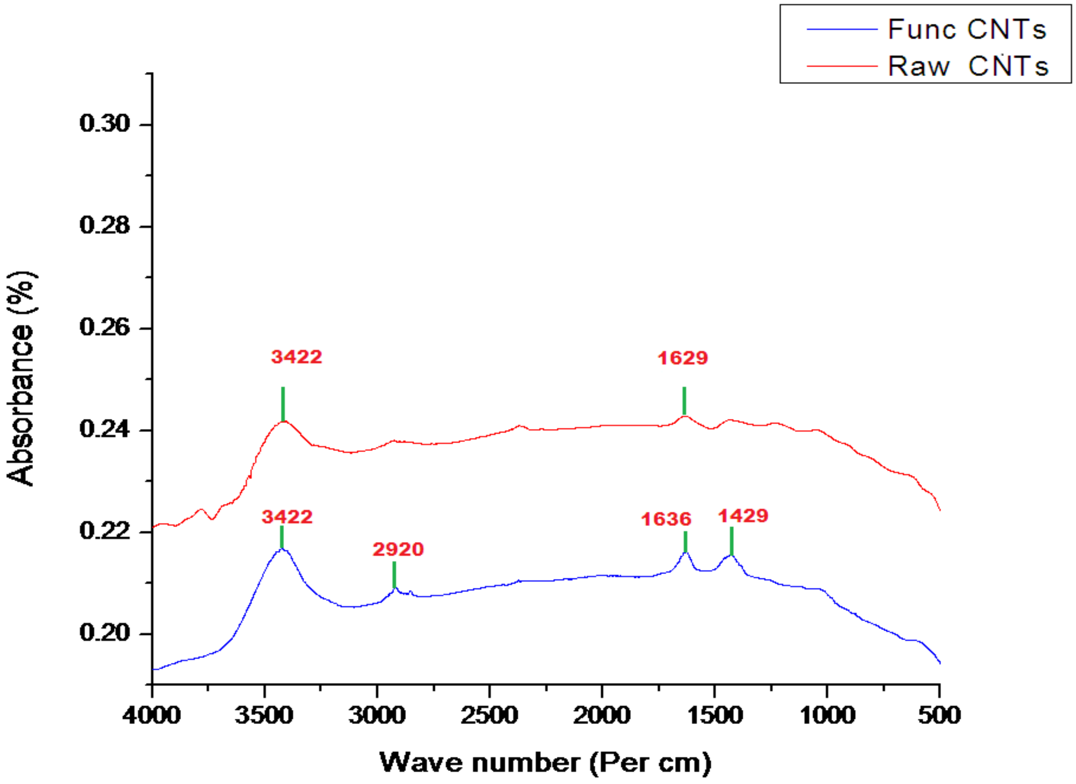


Figure 4.10: FTIR spectrum showing comparison between raw and purified/activated CNTs.

4.2.1.4. TG/DTA

The TG analysis of CNTs presented good indication of the functionality. Activated CNTs with OH and COOH functional groups decomposed earlier than the raw CNTs. The thermal stability of the raw CNTs decreased with increasing by functionalization with Oxygen containing functional groups. The reduction in initial burning temperature of the activated CNTs was closely related to the introduction of the defects and functional groups upon oxidation treatments. That attributed to the earlier decomposition of the grafted carboxylic groups on the nanotubes. For example, the decomposition of the raw CNTs occurred (TGA under 50 ml/minute nitrogen flow, temperature range of 25–1000 ^{o}C, at rate of 15 °C/min) at the onset temperature of 620 ^{o}C while of activated CNTs, it occurred at 600 ^{o}C [18]. Same is shown in the figure 4.10.

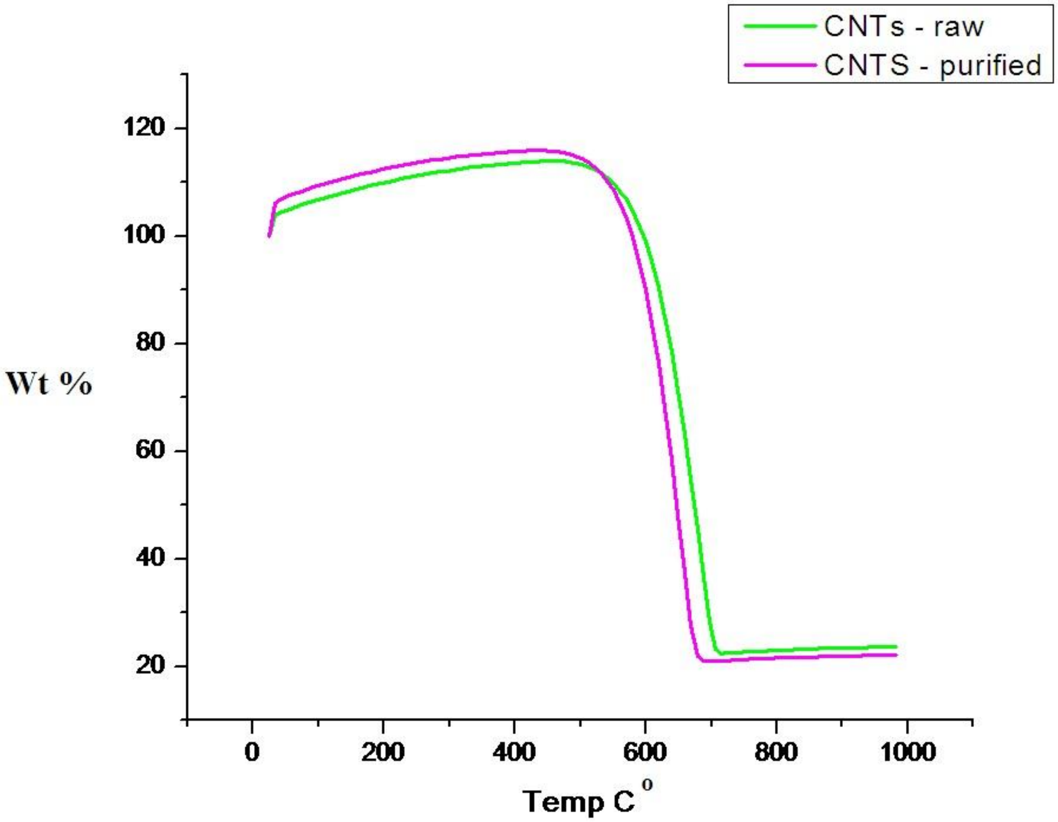


Figure 4.11: TGA curves for raw and purified CNTs.

4.2.2. Findings – Purification Process

Purification of CNTs by sonication in Nitric acid caused to remove entangled Ni residual nanoparticles and also to remove amorphous carbon. This process did not produce defects on tubes bodies but by refluxing in nitric acid. However caps of these tubes were broken off and further Ni particles from inside the tubes were removed. Important findings are as follow.

- In addition to removal of Ni particles OH and COOH functional groups were attached to the body and ends of tubes, thus making these CNTs more dispersed in nature, eliminated their agglomeration permanently and also increased their solubility in polar solution [17].

- Number of functional groups depends on the duration for which CNTs were refluxed in HNO_3 and also depends on concentration of the acid, used. For greater treatment time more functional groups were attached to the CNTs. However by intense reflux for 8 to 72 hours caused defects and shortening of tubes length by breaking it.
- Purification and activation of CNTs through grafting OH and COOH functional groups also affected thermal stability of these tubes. So that functionalized CNTs were oxidized earlier as compared to raw CNTs due to introduction of carboxylic functional groups and defects but the decrease in decomposition temperature may not be so drastic, normally decreases from 10 ^{o}C to 50 ^{o}C was observed in overall temperature range.

4.3. Synthesis of Fe-CNTs Nanocomposite

In the third and last phase of experimental work a nanocomposite material was synthesised as mentioned the detailed procedure in section 3.3, chapter 3. Doping of Fe nanoparticles was done and samples were characterized.

4.3.1. Analysis of Data – Doping Process

In order to characterize doped CNTs samples and analyse the data, EDS, FE-SEM, FTIR, TG/DTA and XRD analytical techniques were used. Result detail of each technique is as under.

4.3.1.1. EDS Spectrum

EDS measurements were used to determine the concentration of Fe particles on the surfaces of activated CNTs. Since the ignition of doped CNTs occured at 16 % Fe and maximum ignition is achieved at 32% Fe by wt., therefore data for only these 2 samples is tabulated.

Table 4.3: EDS Spectrum of Doped CNTs with Fe Particles.

Elements	Doped CNTs - S6c		Doped CNTs – S8c	
	wt.%	Atomic%	wt.%	Atomic%
C K	64.69	78.24	49.29	70.73
O K	19.42	17.63	17.73	19.10
Fe K	15.89	4.13	32.22	9.94
Ni K	-	-	0.77	0.23
Total	100.00		100.00	

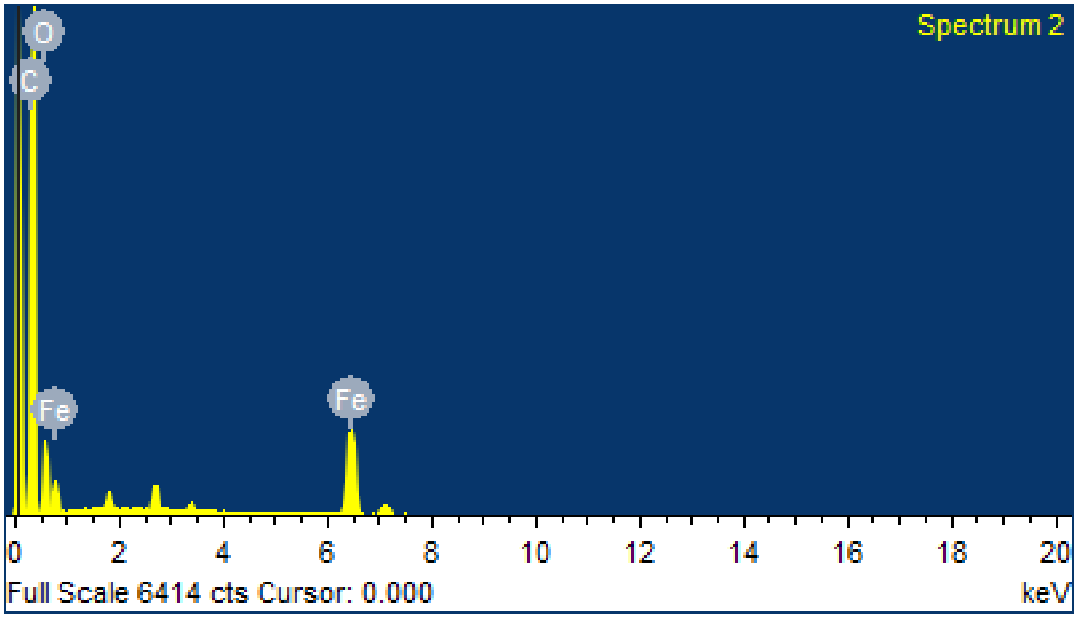


Figure 4.12: EDS spectrum of doped CNTs with 16% Fe by wt.

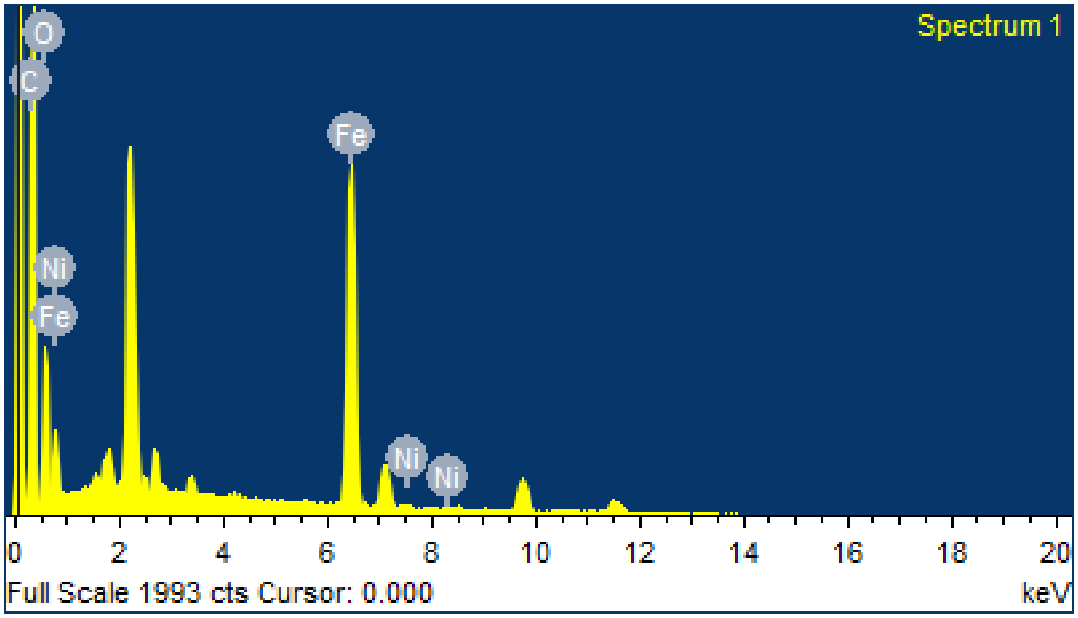


Figure 4.13: EDS spectrum of doped CNTs with 32% Fe by wt.

4.3.1.2. FE-SEM Results

Following SEM images show that after doping of Purified CNTs, two changes in the morphology of the CNTs occurred; one, due to adsorbed Fe/ Fe Oxides nanoparticles the tubes diameters had increased and secondly doped CNTs got more agglomerated as compared to purified CNTs. In addition to this some sort of deformation could also be observed in CNTs body.

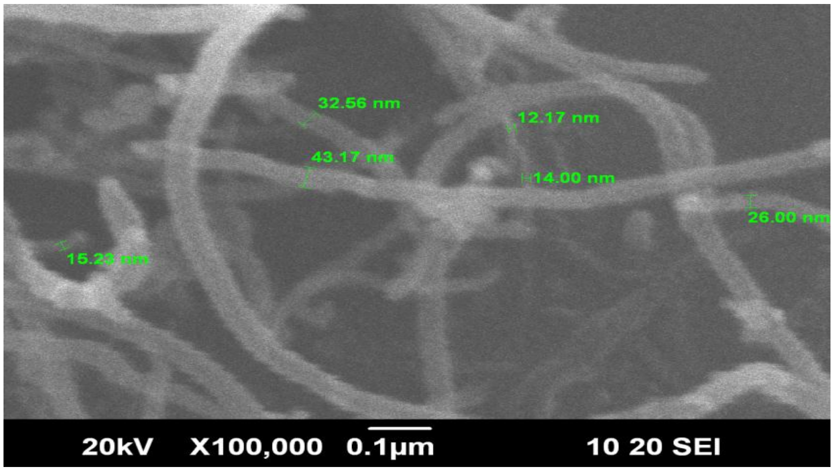


Figure 4.14: SEM image of purified CNTs.

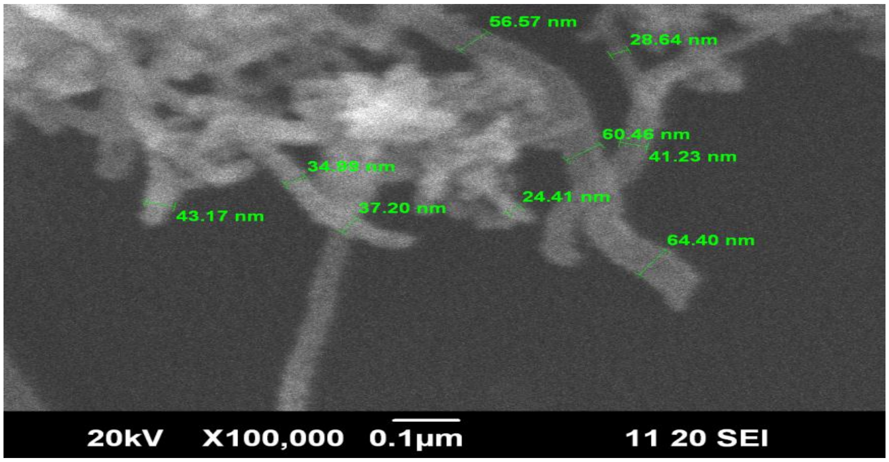


Figure 4.15: SEM image of doped CNTs.

During experimental work pure Fe powder in micro range size was also mixed in different wt. ratios up to 50% by wt. but no ignition was observed. Even the mixture of CNTs and Fe powder was grinded well but no result was achieved. SEM image shows the particles size in the given image. This shows that for ignition of CNTs tubes by photo flashing pure Fe metal must be doped in Nano size only.

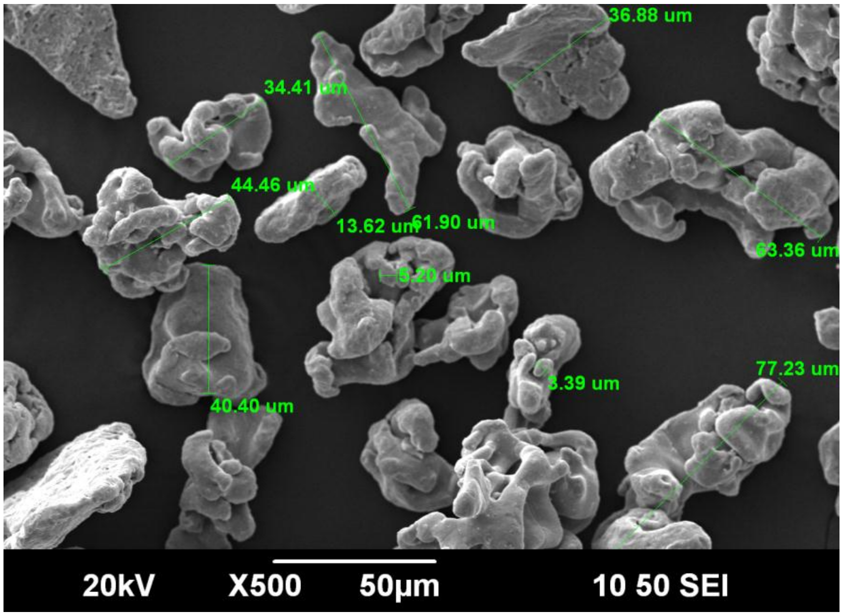


Figure 4.16: SEM image of micron size Fe powder.

4.3.1.3. TG/DT Analysis

TGA was used to determine the role of Fe concentration in decomposition of Fe-CNTs nanocomposite. TGA curves under nitrogen environment as shown in Figure 4.15 indicates that initially wt. of raw CNTs increased up to 10% due to adsorption of N_2 on CNTs surface at the temperature range of 600 °C and then complete decomposition occurred at 700 °C with 80 % wt. loss. The wt. gain in sample with 16% Fe concentration was about 5% up till 350 °C . Then the sample begain to degrade with moderate rate till 440 °C because of the presence of Fe and Fe Oxides particles. Then its rapid degradation started by oxidation of CNTs and stops at 580 °C. Similarly in sample with 32% Fe, started losing its wt. up to 5 % till the temperature reached at 300 °C due to loss of moisture and at 420 °C its rapid decomposition started and ended up at 550 °C with 55 % wt. loss.

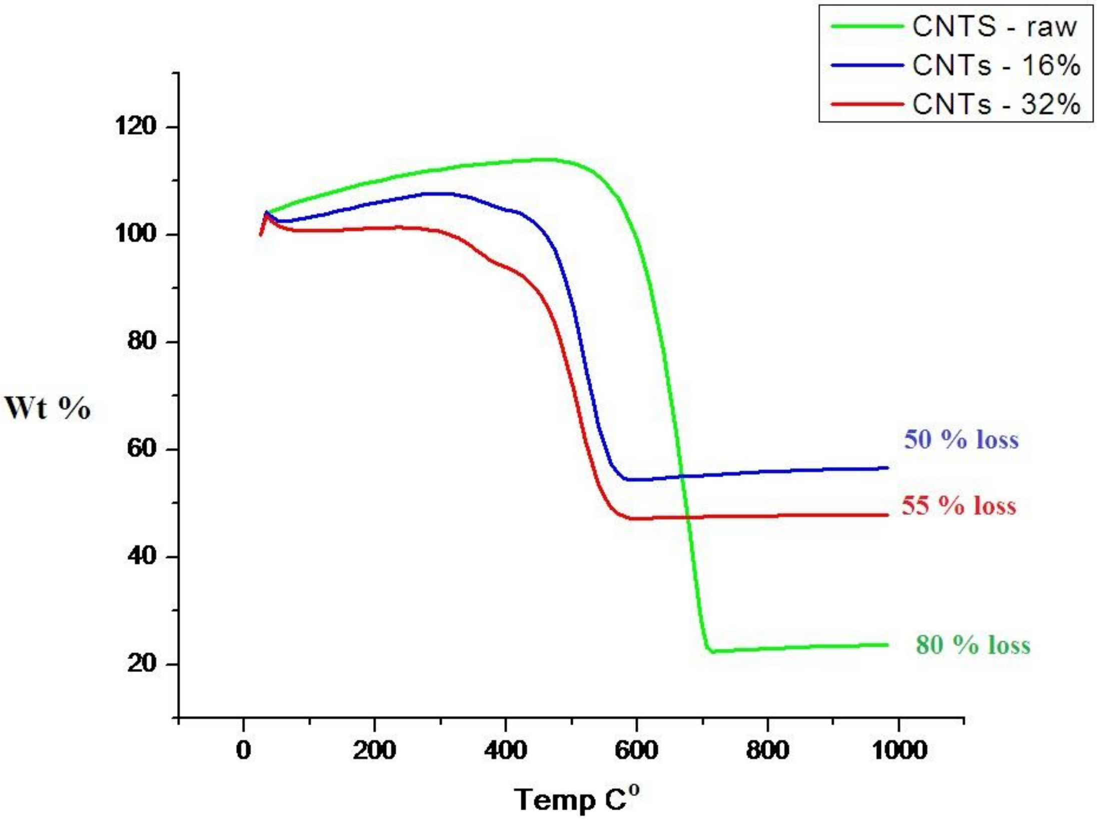


Figure 4.17: TGA curves showing decomposition of CNTs in N_2 environment.

In the same way TGA curves in Figure 4.16 show that the wt. loss in each sample with 16% and 32% Fe concentration was about 5% up till 300 ^{o}C temperature in air environment. That basically happened due to removal of absorbed moisture content. Then these samples begain to degrade with moderate rate till 370 ^{o}C because of the presence of Fe and Fe Oxides particles in the composite . After complete oxidation of these metal particles the samples again got a bit stable till temperature reaches at 410 ^{o}C, where its rapid degradation started by oxidation of CNTs. However at temperature 520 ^{o}C and 530 ^{o}C the wt. loss in samples with 16% and 32% Fe concentration were 55% and 52% respectively. It is very obvious that raw CNTs with no concentration of Fe lose only 5 % wt. through out the heat treatment and remained stable within available heating range i.e. up till 550 ^{o}C. Hence Fe concentration made the CNTs prone to decompose at very low temperature, i.e. at about 400 ^{o}C.

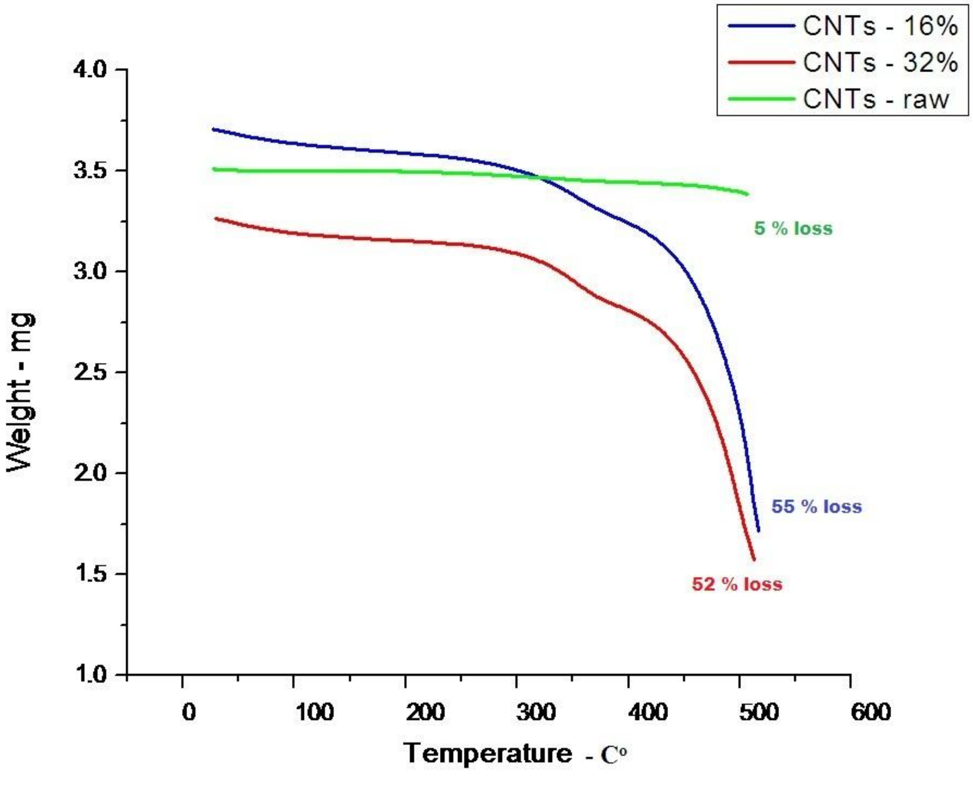


Figure 4.18: TGA curves showing oxidation of the samples in air environment.

DTA curves are shown in the Figure 4.15 below, which shows that the sample with 16% Fe exhibited an exothermic peak at 500 ^{o}C, and sample with 32% Fe concentration displayed an exothermic peak at 480 ^{o}C. Small exothermic peaks at 360 ^{o}C for both samples but prominent for sample with 32% Fe could also be noticed. This shows that it happened due the presence of pure Fe particles on the surface of CNTs. However, it could be seen that sample of raw CNTs showed no peak and exhibited stable heat flow tendency throughout the maximum heating range .i.e. up till 550 ^{o}C. Hence it was proven that by doping the Fe particles on CNTs surface caused it to decompose earlier or in low temperature with releasing heat energy.

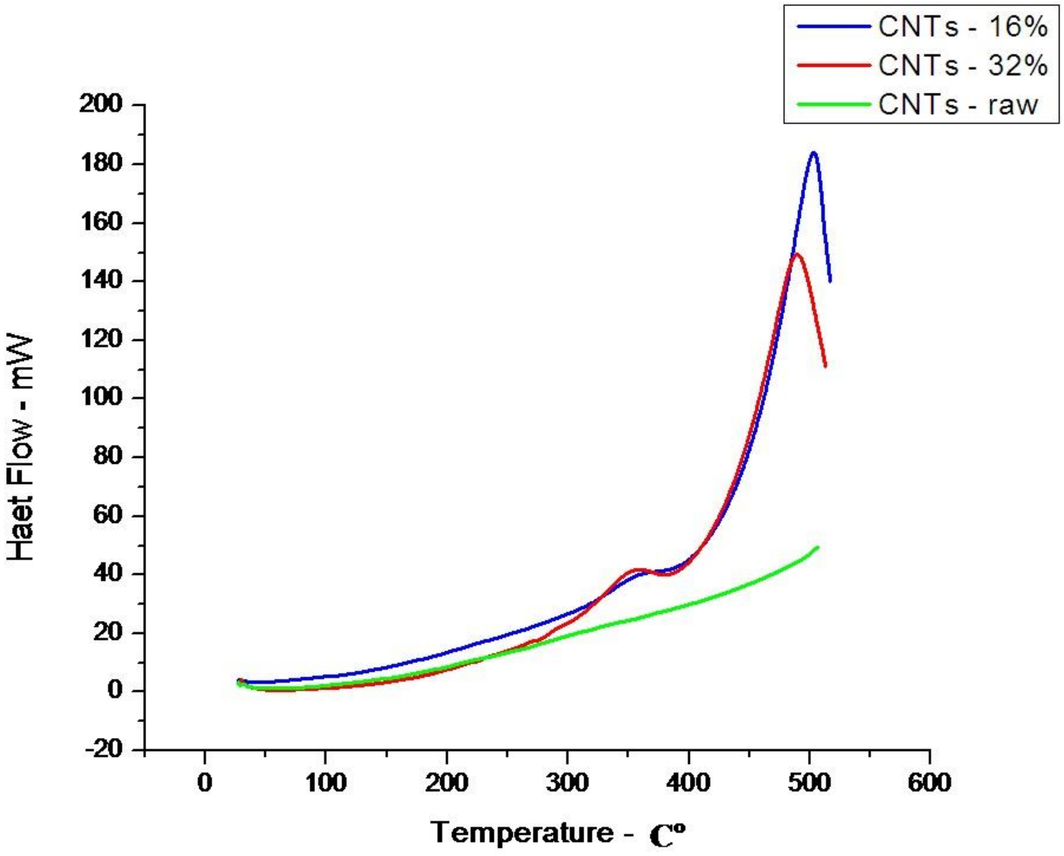


Figure 4.19: DTA curves showing heat flow in the samples

4.3.1.4. XRD Analysis

Figure 14.17 shows an XRD pattern for the purified CNTs. The pattern highlighted the main, broadened and intense peak at 2θ = 25.88^{o}, compared to the normal graphite at 2θ = 26.22^{o} and this corresponded to the (002) reflection. The broadening of this peak represented nano size particles in the structure of CNTs. The other diffraction peaks, were at the angles, 2θ of 42.21^{o} and 44.36^{o}, indexed to (100) and (101) corresponding to graphite, (JCDPS no. 01-075-1621) where as 64.41^{o} indexed to (211) reflections corresponding to nickel/iron residual crystalline (JCDPS no. 01-088-1715).

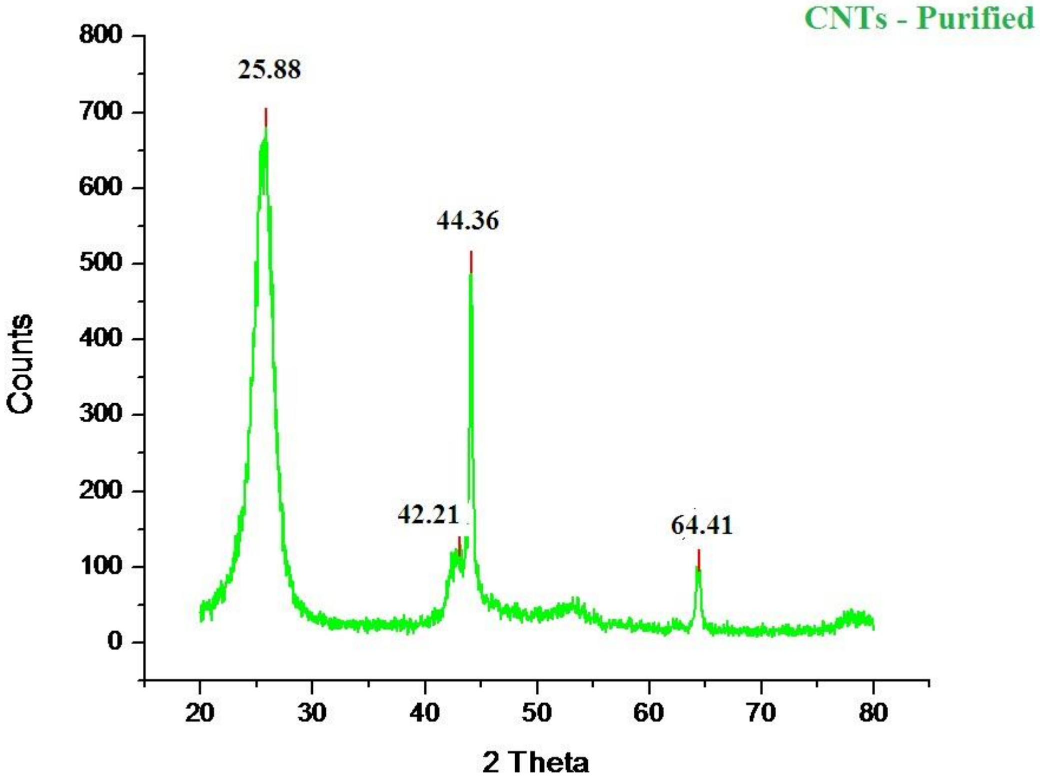


Figure 4.20: XRD pattern of purified CNTs

When graph of doped CNTs with 16% Fe were compared with Purified CNTs, it was obvious from the figure below that the diffraction peaks at 25.76^{o} , 44.55^{o} and

64.37 ° at 2 theta value had got thinned out and strongly reduced in intensity. Similarly in case of CNTs with 32% Fe had been further overlapped by Fe and Fe Oxides nanoparticles even till the extent that peak at 64.37 ° disappeared and intensity of graphite tubes had been reduced to minimum. The possible explanation is that the main peak of nanotubes at 25.88° is masked with the main peak of Fe/Fe Oxides at 25.76° since their positions were so close. Additional is that the crystalline extent of CNTs was lower than the crystalline extent of Fe/ Fe Oxides, leading shielding of the peaks of CNTs. The average crystalline size of Fe particles in the doped CNTs, which was 30.6 nm calculated by applying Scherer formula.

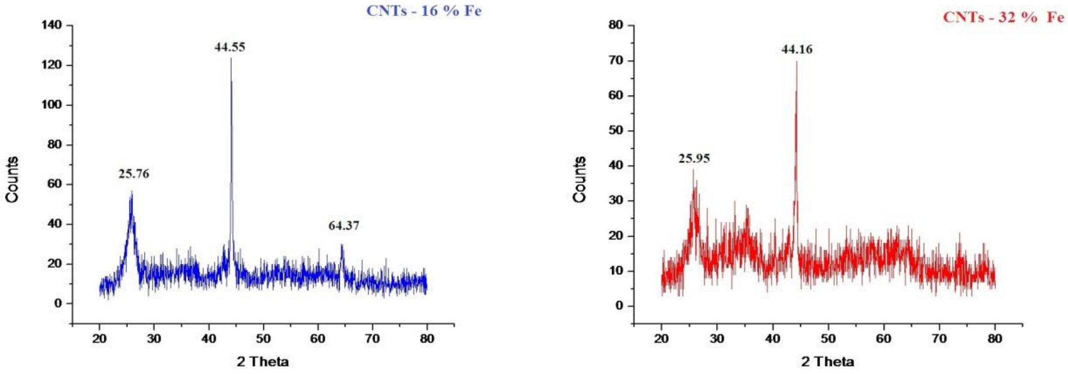


Figure 4.21: XRD pattern of doped CNTs.

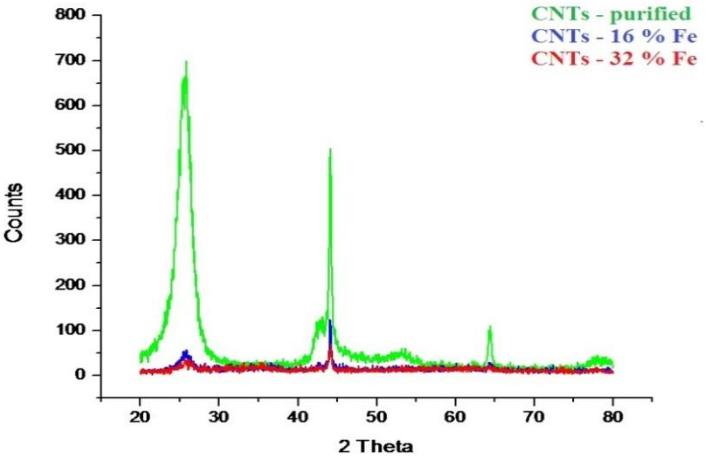


Figure 4.22: XRD pattern showing a comparison of purified and doped CNTs.

4.3.2. Findings – Doping Process

Pure CNTs were quite stable up to 550 ^{o}C or even up to 700 ^{o}C but Fe nanoparticles on CNTs acted as hot spots which caused these tubes to degrade at about 450 ^{o}C. Initially some of these nanometals were oxidized by heating at 300 ^{o}C to 370 ^{o}C and releasing sufficient energy to start with ignition of CNTs at 450 ^{o}C. Important findings are stated below.

- Thus it was proven that these metal particles were only impregnated to the surface of tubes, where these had maximum surface area exposed to flashing/heating and air contact for better oxidation. Therefore these nanoparticles must not be doped in excess concentration in order to avoid its own agglomeration as well as covering of CNTs surface area and reducing its sensitivity to flashing.
- By doping of Fe particles with CNTs, some metals nanoparticles were adsorbed on the tubes surfaces by reacting with functional groups i.e. OH and COOH and converted into FeO, Fe_2O_3 and Fe_3O_4. However some Fe nanometal particles adsorbed in form of pure metal. Only these pure Fe nanoparticles caused the CNTs to ignite by applying photo flashes.
- It is also important to highlight that for low temperature oxidation of CNTs, only nano size Fe particles must be adsorbed on the body of CNTs, where as pure Fe particles in micron size did not play any role to ignite CNTs by photo flashing. Smaller the nano size of Fe metal on the tubes, easier will be its ignition by photo flashing.

Chapter 5: Applications, Conclusion and Recommendations

5. *This chapter deals with salient features of the study, its application, final out come/conclusion and recommendations regarding future prospects of the research work.*

5.1. Salient Features of the Study

- The photo flashing effect on the raw or as received CNTs was studied by subjecting three different types of MWCNTs to a camera photo flashes.
- Out of these three types, a raw CNTs with minimum surface area and maximum density were selected as reference material for our further study and research.
- The selected CNTs were purified from residual nano Ni particles of synthesis and amorphous carbon by wet oxidation through sonication and reflux in 70 % concentrated HNO_3, centrifuge, washing and heat treatment process.
- Purification was achieved along with the activation of CNTs by grafting hydroxyl (OH) and carboxylic (COOH) groups on the surface of theses tubes, which made these tubes well dispersed, soluble in polar solvent and prone to dope with Fe nanoparticles.
- In this study ferrocene was used as an iron precursor. It was dissolved in toluene with increasing ratio each time but quantity of CNTs was kept constant. Same solution was sonicated and then toluene was evaporated by using rotary vacuum evaporator.
- CNTs/ ferrocene mixture was calcinated at 210 ^{o}C in vacuum oven for 3 hours and CNTs decorated with Fe nanoparticles on its surface were produced.
- After grinding the product a nanocomposite material was achieved, which wass analysed by using various analytical techniques, including, EDS, FE-SEM, FTIR, TG/DTA and XRD.

- The final product wass subjected to camera photo flashing and its ignition was achieved. To further enhance its combustion sodium perchlorate monohydrate was added, which did not caused violent combustion when it is exposed to a photo camera flashes due to presence of moisture.
- The intensity of photo flash was determined as 14 Mw/cm^2 by using light/lux metre.

5.2. Applications of Nanocomposite Material

Fe-CNTs nanocomposites is a new material with interesting properties that not only combines the properties of CNTs and Iron /Iron Oxide together but also exhibits some new characteristics by their mutual combination. Moreover, by combining of these materials in a composite can over come some dis advantages, e.g. Iron/Iron oxide Nanoparticles have a tendency to agglomerate because of their dangling bonds. In the composite material, dispersion of the Nanoparticles on the surface of the Nano tube reduces its agglomeration. It is worth mentioning that the aggregation of nanotubes in aqueous media is resolved by functionalization of nanotubes and these CNTs may be used as carrier to stabilize the Fe nanoparticles and maintaining their integrity. Few important applications of synthesised nanocomposites material as nEM are highlighted as under.

5.2.1. Application of nEM

When the nanocomposite material is applied in close contact with an oxidant i.e. Sodium perchlorate monohydrate and porous silicon film, a high exothermic reaction produces large amount of heat, gasses and pressure. Thus nEM is fabricated, which may be utilized in the following ways.

- It can be used as a smart initiator or primer to initiate the separate conventional or non explosive through remote optical initiation.
- It can be used as a source of high energy and pressure since enough volume of gasses is generated by its complete oxidation.

- It may also be used as bobby trap for military purpose being undetectable easily due to very small in size.
- Due to vey small in size relatively small area of a device can be heated, burned or melted, with no or less impact to the surrounding area, e.g. micro welding application.
- It can be used for steering purpose to steer the orientation and ballistics of a micro device, especially in space technology.
- It can also be used as a source of heat to boil or heat up a liquid, adsorbed on an electronic chip for further analysis.
- In addition to optical means the nEM can also be initiated through different means, including electric, thermal and a laser pulse, which makes it very versatile in use and nature.
- Being self sufficient, the nEM can be used in environment no oxygen.

5.2.2. Nanocomposite as Magnetite

When CNTs is doped with ferrocene and then calcined in air instead of vacuum environment, the resultant CNTs is impregnated by Fe_3O_4. Thus a Nano Ferro magnetic composite is produced. Ferro magnet is easily magnetized, but it gives up most of its magnetization when taken away from the magnetic field, these species are also known as soft magnetic materials. Few applications are as under.

- The magnetite CNTs is used for europium adsorption. Europium is a dopant in some types of glass in lasers and other optoelectronic devices. Europium oxide (Eu_2O_3) is widely used as a red phosphor in television sets and fluorescent lamps [27].
- The composite is used as an adsorbent for removal of various elements from water such as Pb, Cu, Ni, Sr and Cr.
- Magnetic nanocomposite has also been utilized as an adsorbent for removal of cationic dyes from aqueous solution [18].
- This composite is also used in magnetic field sensors to read the data on magnetic disks, tape and in antilock brakes.

5.2.3. Nanocomposite as Sorbent

By adopting the same Technique different metal/metal oxides can be decorated on CNTs surface while utilizing suitable solvents and precursors. Thus the nanocomposite introduces chemically an inert surface with greater specific surface area for physical adsorption. This type of nanomaterial has relatively uniform structure, thus more adsorption sites are provided. Few examples are as under.

- MWCNTs/ Al_2O_3 nanocomposite is used an effective sorbent to remove lead ions from aqueous solution.
- Manganese oxide Decorated CNTs can be utilized for the removal of lead from an aqueous solution.

5.3. Conclusion

- So far, photo ignition of only SWCNTs has been reported due to its large surface but here by this research study it is proven that photo ignition of MWCNTs can be achieved by decorating these tubes with Fe particles.
- Purification and activation of raw CNTs are must for synthesis of nanocomposite material.
- Photo flash ignition of nanocomposite material is achieved by doping MWCNTs with minimum 16% Fe particles by wt., less than that ignition is not possible. Moreover ignition is only attainable when Fe particles, decorated on CNTs surface are in form of pure and Nano size particles.
- Maximum photo flash ignition efficiency is achieved with doping of 32% Fe particles by wt. Above this percentage the particles get agglomerated and its less surface area is exposed to air contact.
- For easy ignition the doped CNTs must not be compacted and these tubes must have maximum surface area in contact with air at the time of light flashing.
- With increasing photo flash intensity the ignition of nanocomposite material can be attained even on single photo flash.

- With increasing Fe concentration on CNTs, its the thermal stability decreases and heat of combustion increases drastically.
- This method is employed for synthesis of a nanocomposite of CNTs impregnated with Fe/ Fe Oxides and is a versatile technique in which various metal/metal oxides can be decorated on CNTs surfaces by utilizing suitable solvents and metal precursors, while applying right calcination temperature of each precursor.
- Very low intensity of energy that is ca. 14 mW/cm^2 caused the ignition of the Fe-CNTs nanocomposite as compared to the previous work. In which Bruce Chehroudi found the energy of ignition of SWCNTs ca. 10 to 150 W/cm^2 and Ajayan et al. determined it earlier as 100 and 300 mW/cm^2.

5.4. Recommendations

MWCNTs exhibit extra ordinary properties which make them suitable for various application in electronics, medicine, polymers and catalysis. The exceptional thermal, electronic and mechanical, properties as well as the possibility of their internal and surface modification by doping with different metals and activation further increase its applications many folds. Keeping in view the future prospects of this research study following points are recommended.

- Doping process of Fe/ Fe Oxides may also be done through auto clave technique and various factors affecting the process need to be analysed.
- Fe Doping on CNTs with different diameter and density need to be probed out according to each type of tubes.
- Calcination process of precursor, doped with CNTs may also be done in nitrogen and air environment, in addition to vacuum and a comparative study is required to be presented for each case.
- Without activation of CNTs by introducing functional groups on their surfaces, doping process can be done and results need to be analysed.

- Role of photo flash intensity for ignition of Fe-CNTs composite needs to be analysed by applying various types and strength of Camera flashes/laser pulses.
- Nanocrystalline size of doped Fe particles for maximum and minimum efficiency level is required to be probed out.
- Instead of Toluene, different solvents and their effects on doping process may also be worked out.

References

[1] P. Chaturvedi, P. Verma, A. Singh, P.K.Chaudhary, Harsh, P.K. Basu, Defence Science Journal, 58 (2008) 591.

[2] Mintmire, J.W. Dunlap, B.I White, Physics Review Letter, 68 (1992) 631.

[3] Dekker, Physics Today, 52 (1999)22.

[4] Popov, M. kyotani, M. Nemanich, R. Koga, Physics Review, 65 (2002) 033408.

[5] Sanders, Press Release, (2003).

[6] Lu, X. Chen, *Chemical Reviews*, 105 (2005) 3643.

[7] Hong, S. Myung, *Nature Nanotechnology*, 2 (2007) 207.

[8] F.J. Xiao, X.L. Yu, F.F. Feng, X.A. Sun, X.F. Wu, Y.J. Luo, Journal of Inorganic and Organometallic Polymers and Materials, 23 (2013) 315.

[9] Thostenson, E. Li, C. Chou, *Composites Science and Technology*, 65 (2005) 491.

[10] Mingo, N. Stewart, D. A. Broido, D. A. Srivastava, Physics. Review, 77 (2008) 033418.

[11] M. Lopez-Lopez, J.C. Bravo, C. Garcia-Ruiz, M. Torre, Talanta, 103 (2013) 214.

[12] S.H. Tseng, N.H. Tai, W.K. Hsu, L.J. Chen, J.H. Wang, C.C. Chiu, C.Y. Lee, L.J. Chou, K.C. Leou, Carbon, 45 (2007) 958.

[13] C.D. Malec, N.H. Voelcker, J.G. Shapter, Materials Letters, 64 (2010) 5117.

[14] M. R. Manaa, A. R. Mitchell, R. G. Garza, P. F. Pagoria, B. E. Watkins, Journal of the American Chemical Society, (2005) 212655.

[15] A. Vignes, O. Dufaud, L. Perrin, D. Thomas, J. Bouillard, A. Janès, C. Vallières, Chemical Engineering Science, 64 (2009) 4210.

[16] S. K. Pillai, L. Matlhoko, C. Arendse, S. S. Ray, M. Moodley, Applied Physic A Material science and processing (2000).

[17] R. Yudianti, H. Onggo, Sudirman, Y. Saito, T. Iwata, J. Azuma, The Open Materials Science Journal, 5 (2011) 242.

[18] V. K. Gupta, T. A. Saleh, Carbon nanotubes - From Research to Applications, 17 (2011).

[19] F. Zhao, H. Duan, W. Wang, J. Wang, Physica B: Condensed Matter, 407 (2012) 2495.

[20] M. Stancu, G. Ruxanda, D. Ciuparu, Optoelectronics and Advanced Materials - Rapid Communications, 5 (2011) 846.

[21] M.N. Tchoul, W.T. Ford, G. Lolli, D.E. Resasco, S. Arepalli, Chemistry of Materials, 19 (2007) 5765.

[22] A. Mahajan, A. Kingon, Á. Kukovecz, Z. Konya, P.M. Vilarinho, Materials Letters, 90 (2013) 165.

[23] B. Scheibe, E. Borowiak-Palen, R.J. Kalenczuk, Materials Characterization, 61 (2010) 185.

[24] A.-R. Leino, M. Mohl, J. Kukkola, P. Mäki-Arvela, T. Kokkonen, A. Shchukarev, K. Kordas, Carbon, 57 (2013) 99.

[25] L. M. Currano, M. Dubey, R. G. Polcawich, Carbon nanotubes Explosives, 0206290 (2013).

[26] W. R. May, Solubility of Ferrocene in Organic Solvents, (2001).

[27] M. T. Montgomery, R. B. Coffin, T.J. Boyd, J.P. Smith, S.E. Walker, C.L. Osburn, Environmental Pollution, 159 (2011) 3673.