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Synthesizing of helical-single walled carbon nanotubes by chemical vapour decomposition for engine

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ABSTRACT

The captivating interest on carbon nanotubes (CNTs) has kindled the research activity after its discovery in 1991. It is due to its fabulous properties which have opened numerous applications like high weight to strength ratio, field emission transistors, and catalysis. Irrespective of the stunning technological development there is still much struggle in the synthesis aspect, which is a great drawback in compliance of these unique materials in the commercial application. Apart from various known method catalytic chemical vapor deposition (CCVD) is more advantages, where SWCNTs can be produced with varying diameters, large scale production, with high purity, variable temperature and most importantly it can be produced economically. In CCVD technique, We have used magnesium metal as a substrate with transition metal like Fe, and Ni, to prepare combustion catalyst. SWCNTs synthesized from FeaNibMg1-(a + b)O (FNM) catalyst had a higher yield than other catalysts with helical structure in the single layer of graphitic carbon (h-SWCNTs). The morphology of the synthesized h-SWCNTs was identified by Field Emission Scanning Electron Microscope and many others. Environmental damage from industries is looking for a prominent candidate to sort out the issues such as high catalytic activity, reusability, and stability norms. With the obtained result a comparative study was done against combustion catalyst, purified and pristine SWCNTs. It is found that the pristine h-SWCNTs had a good photo catalytic activity with this result we have confirmed SWCNTs synthesized from solution combustion technique can be utilized for commercial application.

1. Introduction

Carbon is not just because of life process it is required, is an astonishing element but the existence of it in numerous forms of allotropes also. Moreover by synthesis of carbon it can be formed many myriad of structures like nanotubes and others. Now a day's carbon in the form of nanotubes (CNTs) plays, dominant role in industrial, scientific and nanotechnological research. In few decades carbon nanotubes has acquired central attraction in nanoscience domain [1]. There is no doubt, that now a day's among all the field of research nanotechnology are synthesis, characterization and applications of CNTs is one of the most active field, which obviously led to a recommence the interest in synthesizing of many different form of carbon nanomaterials like, helices, fibers and graphene etc. [2]. Because of the morphology diversity of carbon which allows the flexibility during alteration of the properties. Nanomaterial having nonlinear or helical morphology[1] shown in Fig. 1. The reported nanomaterial were first consider the effort for curiosity which was focused on their prevention rather than the synthesis. After long time in 1990 s it again stimulated after discovery of carbon nanotubes, which led to the attention in the carbon fibre and tubes shown in Fig. 2 [3], mostly with abnormal morphology like helics, spring etc. and it was expected that nanomaterial which having helical morphology should have unique and similar both chemical and physical properties of their macro component also. The formation of carbonaceous material in helical form from carbon precursors in presence of catalyst by using bottom up approach it is likely to move by similar procedure used for synthesizing straight tubes [2,4].

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Nomenclature

Å	Angstrom (1exp.-10)
TPa	Tera Pascal (unit)
GPa	Giga Pascal (unit)
sccm	standard cubic centimetres per minute (unit)
ºC	Degree Celsius
nm	nano meter (unit)
W/mk	Watts per meter Kelvin
Scm-1	Siemens per centimetre
TA	Thermal Analysis
cm	centimetre
HCl	Hydro Choleric Acid
FCM	FexCyMg1-(x + y)
FVM	FexVyMg1-(x + y)
NCM	NixCyMg1-(x + y)
XRD	X-Ray powder Diffraction
FESEM	Field Emission Scanning Electron Microscope
EDAX	Analysis
HRTEM	High-Resolution Transmission Electron Microscopy

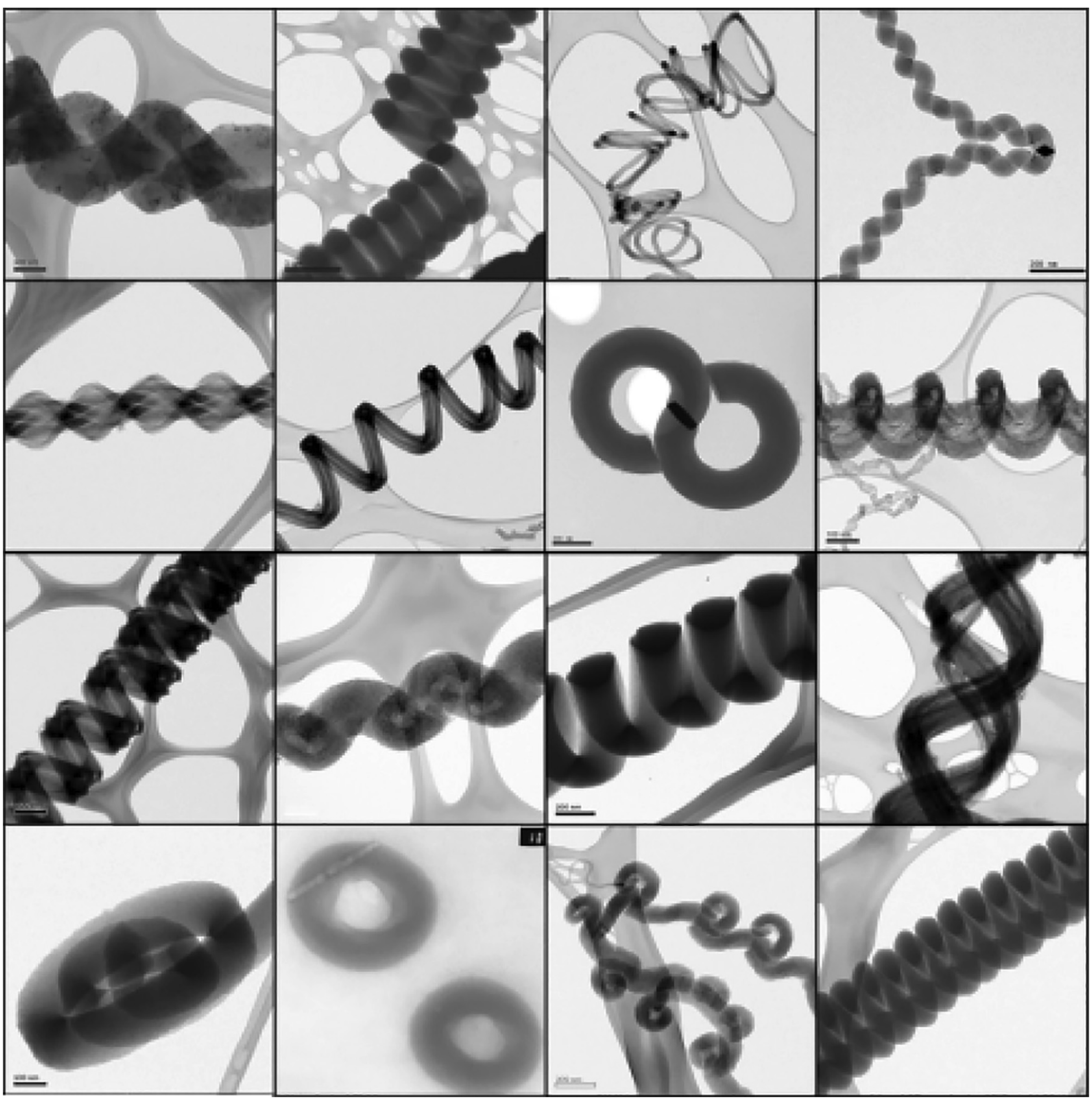

Fig. 1. Various Non-linear morphology of carbon nanotubes.

1.1. Helicity in single walled carbon nanotubes

Generally, helical nature of single walled carbon nanotubes (SWCNTs) is thought may because of uneven extrusion shown in Fig. 3, of carbon through a catalytic surface, which gives rise the curvature in SWCNTs shown in Fig. 4. Catalyst composition and external stress directly may affect on helical nature of SWCNTs. As an alternate Zhang et al. [2] suggested that helical carbon fiber which is formed from the catalyst that may be affected by Van-der wall forces which exist in between surrounding and carbon fiber.

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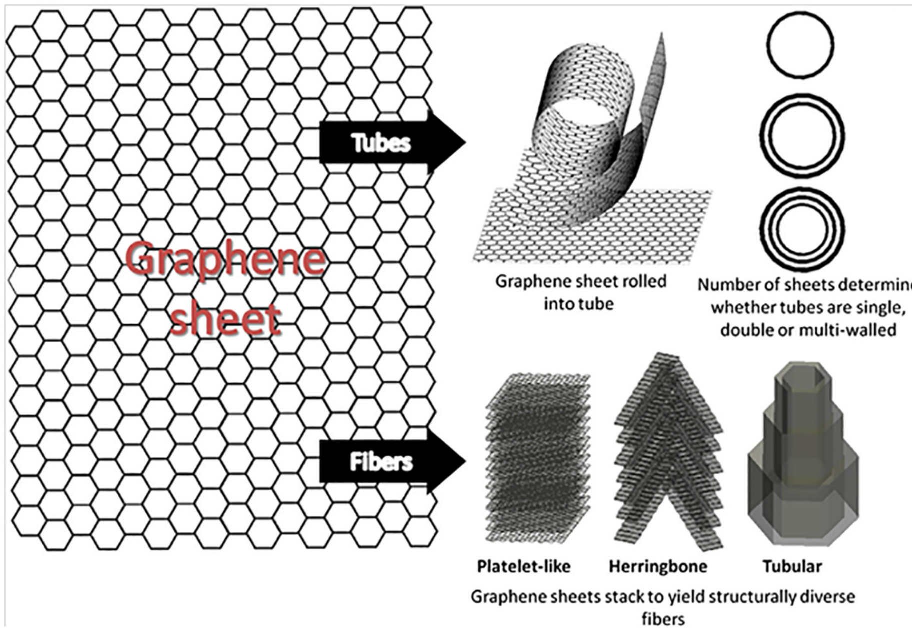

Fig. 2. various morphology of carbon nanotubes by arranging graphene sheet.

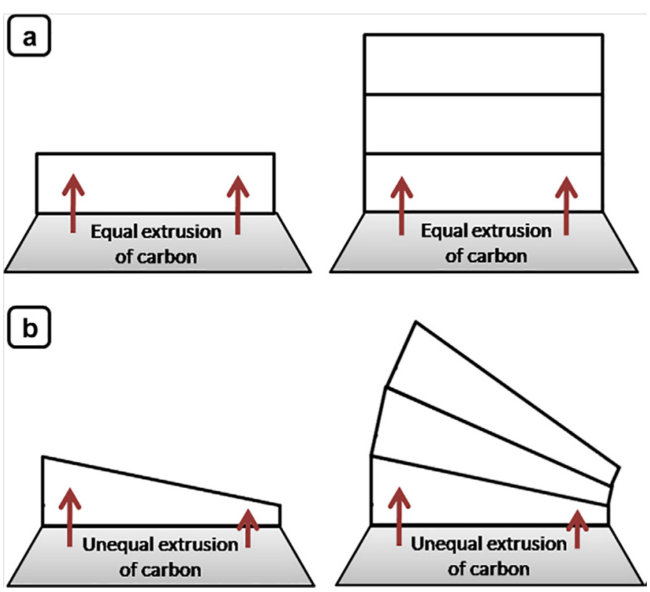

Fig. 3. (a) straight fiber is the results of equal extrusion (b) non-linear fiber is the result of unequal extrusion.

1.2. . Carbon helics growth characteristics

Many investigator investigated by inserting the polygon like pentagon or hexagon ring within lattice of the tubes or from catalytic surface unequal extrusion of carbon fiber [4]. However how this phenomena are interlinked is yet to completely understood. Till date mostly researchers focused on the composition and catalytic morphology for the evolution of helical carbon tubes.

1.3. Effect of catalyst morphology

Till date researcher are yet to emphasize completely for the relationship between the size and type of used catalyst and the size and type of carbon nanostructure formed. It was observed that the point of growth of SWCNTs is associated with the catalytic grain size. Apart from this it was also found that two major issues encountered which are (i) the regularly faceted shape of the catalyst and (ii) size of the catalyst particle and the type of carbon formedwith it. The growth of helical-SWCNTs can be controlled by controlling the catalyst particle size[5,6].

Zhang et al.[2] found that at 250 °C carbon nano fiber formed by using nano Cu catalyst, the size of the catalyst were in between 10 and 30 nm in radius and only straight carbon fiber were formed when catalyst size was greater than 60 nm in radius.

2. Manufacturing

Helical-Single Wall Carbon Nanotubes (h-SWCNTs) is used in many applications either accumulated as very thin film or dispersed in powder form. However, h-SWCNTs product for commercial purpose are still very difficult so their execution can be accomplished by combining the conventional formation procedures. Due to various researchers working on SWCNTs, so fabricating process is getting advanced continuously. Wang et al. investigated that composite of carbon nanotubes (CNTs) having multi-functionalities, such as higher electrical conductivity, greater Young's Modulus and high strength. They found these properties along the length. higher volume fraction, very good molecule alignment, in co-existence and having less waviness of the CNTs and a novel fabricating procedure for commercial purpose production [7,8].

2.1. Experimental procedure

2.1.1. Materials

The gases used in the synthesizing of h-single walled carbon nanotubes are Acetylene, Nitrogen and hydrogen in which Acetylene having purity of 99.9% is used as carbon source, Nitrogen having purity of 99% is used as carrier gas while hydrogen of 99% purity is used as a reducing agent. For purification of h-single wall carbon nanotubes commercial grade hydrochloric acid is used. For solvent double distilled water is used. All the used chemicals are of analytical grade and hence used without filtering it.

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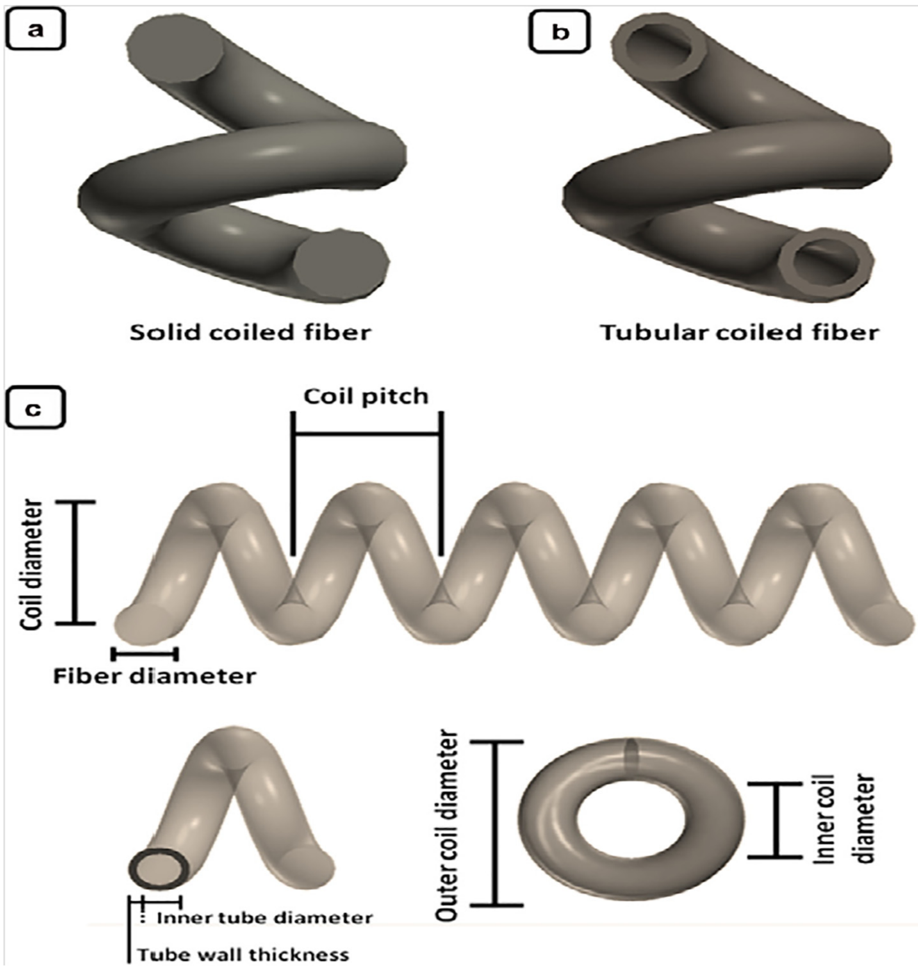

Fig.4. simplified representation of (a) solid coil (b) tubular coil and (c) defining parameters of the coil fiber.

2.2. Synthesis of combustive catalyst

2.2.1. Synthesis of FNM catalyst

The solution combustion synthesis technique is used for synthesizing the combustive catalyst $Fe_aNi_bMg_{1-(a+b)}O$ (FNM). Magnesium Nitrate, Nickel Nitrate and Ferrous Nitrates are used in stoichiometric form $Fe_aNi_bMg_{1-(a+b)}O$ (FNM). Various molar composition form such as $Fe_{0.25}Ni_{0.10}Mg_{0.65}O$ (FNM-a), $Fe_{0.20}Ni_{0.15}Mg_{0.65}O$ (FNM-b), and $Fe_{0.15}Ni_{0.20}Mg_{0.65}O$ (FNM-c), is prepared by keeping constant molar ratio of Magnesium Nitrate [9,11].

3. Synthesis and purification of single wall carbon nanotubes

3.1. Schematic diagram of chemical vapour deposition apparatus

The helical-single wall carbon nanotubes are synthesized by the technique of Combustion Catalyst by Chemical Vapour Deposition (CVD). CVD apparatus contains a tube horizontally which having heating filament along with a program controller for controlling the required temperature for reaction. Mass flow meter and various gas sources are connected with the horizontal tube which is made up of alumina, as shown in Fig. 5. A schematic diagram of chemical vapour test apparatus for synthesizing h-SWCNTs is shown in Fig. 5. The tube having input and output terminals. For maintaining the temperature the filament is winded all around the tube. By the use of programmable controller which is placed at the center of the tube, temperature is maintained. For regulating the mass flow rate of various gasses according to the requirement a digital mass flow meter is attached with the gas cylinder [10,12].

3.2. Synthesis of single wall carbon nanotubes

The combustive catalyst chemical vapour deposition technique is carried out at normal atmospheric pressure in the tube. The

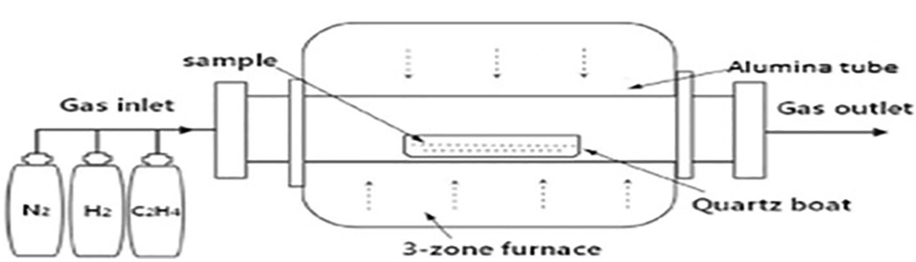

Fig. 5. Chemical Vapour Deposition Apparatus schematic diagram.

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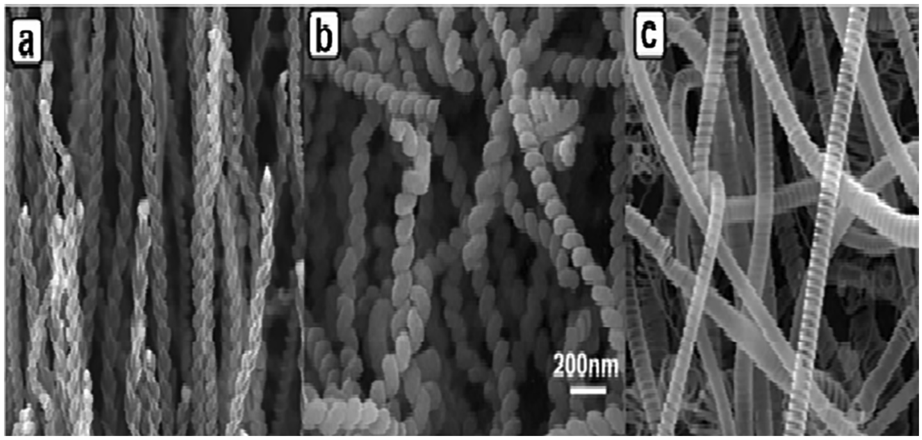

Fig. 6. Types of helical carbon nanomaterials produced: (a) twisted helices (b) tightly coiled helices, (c) spring-like.

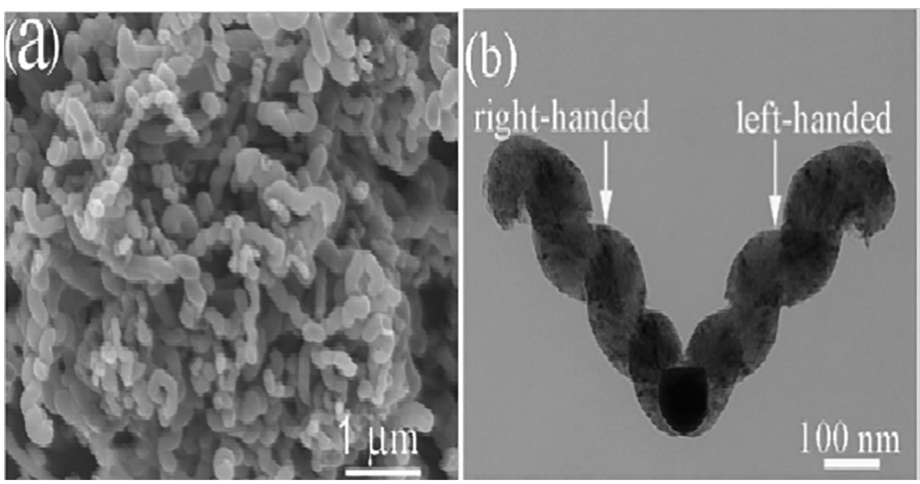

Fig. 7. Typical **(a)** FE-SEM and **(b)** TEM images of helical carbon nanofibers (h-CNTs) [5].

catalytic reaction is for SWCNTs preparation is carried out with various composition of catalyst as formed earlier. Around 100 mg of combustive catalyst is kept on quartz boat which is further kept in center of the horizontal tube. Under the Nitrogen atmosphere the catalyst is heated with the flow rate of 100sccm for decreasing the catalytic surface till inside the tube temperature reaches to 650 °C. Further reaction is carried out by changing the flow rate from 10 to 100sccm at various temperature ranging between 650 °C and 850°Cfor 10 min. After completing the reaction, furnace is allowed to cool to room temperature in the atmosphere of Nitrogen [14].

The mass of the h-SWCNTs deposited by acetylene decomposition is calculated when the catalyst is used by below equation:

$$h - SWCNTsAccumulated(\%) = \frac{Mtot - Mcat}{Mcat} * 100\%$$

where, Mtot is the total mass of acetylene after the completion of reaction and Mcat is the mass of catalyst before starting of the reaction [13].

3.3. Purification of helical-single walled carbon nanotubes

Helical-single walled carbon nanotubes which is synthesized is further treated for purification with hydrochloric acid to remove the particles of metal which are present in FNM catalyst. This process is carried out by stimulating the helical-single walled carbon nanotubes which is synthesized, with concentrated aqueous solution of hydrochloric acid (35–40% by weight) at the room temperature for 45–50 min. After that is solution is drenched and washed by the use of distilled water till product get stable and then helical-Single Walled Carbon Nanotubes is dried out around 80–85 °C for 5–6 h [15].

4. Characterization of Helical-SWCNTs

4.1. Characterization techniques

The phase purity, microstructure and morphology of both the samples are characterized by the use of Transmission Electron Microscopy, Scanning Electron Microscope and Electron Diffraction shown in Figs. 6 and 7 [16,17]. Magnetic properties of the synthesized helical-SWCNTs is investigated at room temperature by Vibrating Sample Magnetometer by applying magnetic field. Scanning Electron Microscopy image is taken by using a Carl Zeiss Auriga SEM-FEB field emission scanning electron microscope. All Scanning Electron Microscope samples are sputter coated with a thin layer of gold to avoid deposition of charge over it.

5. Application

Helical-SWCNTs can be used anywhere, where the CNTs not provides firmly griping or the component which having curvilinear

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shape. Engine having many components which are in irregular in shape so according to the irregularities required we can make by that much extruding. Casing of engine are one of the most important thing in engine which facing various types of load and hence the casing must be stronger. By the use h-SWCNTs in engine, we can fulfill the recent demands regarding the visual and thermal signature, light weight, increased strength to weight ratio, and maneuverability. These demands or necessity can be fulfill by use of h-SWCNTs in engine.

6. Conclusion

During the experiment it was found that in CVD method by controlling the size of the catalyst and carbon source helical single walled carbon nanotubes can be formed in bulk quantity for the use in industrial purpose. Hence by careful manipulation of above mentioned factors we can produce the our desired shape and size of helical-single walled carbon nanotubes as when we required. The unique morphology of helical-single walled carbon nanotubes has led to consider for using in various engine parts. While there is various synthesis method, CVD method provide better yield and coil morphological control. The unique mechanical, electrical and absorbance properties of helical-single walled carbon nanotubes make them idea for using in engine parts.

Credit author statement

All work has been done by Indradeep Kumar and supervised by his PhD supervisor Dr. C. Dhanasekaran which is the co-author of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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