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Development of Indigenous under Gas Arc Discharge System for Gram Scale Growth of Carbon Nano-Tubes

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Abstract: In this study indigenous arc discharge setup is designed and fabricated for the gram-scale production of carbon nanotubes. a detailed description of the development and fabrication of the system is given. Carbon nanotubes were synthesized in the presence of Argon gas at 400 -600 Torr Pressure by indigenous setup with different parameter combination like arcing time and role of catalysed is reported analyses of the morphology, composition, and purity were done. The synthesized materials were characterized using scanning electron microscopy, X-ray diffraction (XRD), and Raman spectroscopy. The scanning electron microscopy images show agglomerated tubed fiber like structures in samples from the arc discharge setup, Structural investigations done using powder XRD revealed the presence of the hexagonal crystallographic phase. Furthermore, the presence of the G and 2D bands reveals sp2 hybridization and confirms the presence of carbon nanotubes in samples.

Key words: *CNT, Indigenous arc discharge setup, XRD, SEM, RAMAN*

1 Introduction

Growth mechanism of carbon nanotubes in arc discharge Over the last two decades, researchers have investigated and suggested growth conditions for nanotube formation based on their experimental observations. Despite seminal studies, no clear understanding of the growth mechanism has been developed and a critical study lies in understanding the physics of this mechanism which certainly helps in predicting the optimum growth conditions of nanotubes. In this section, we present an outline of the synthesis mechanism in the growth of CNTs in arc discharge. The two electrodes are brought in contact and upon application of voltage, constant current flows through them. The electric current results in resistive heating and raises the temperature of the electrodes. The anode is moved back to maintain a desired gap (~1 mm) between the electrodes for continuous deposition of carbon vapours. Meanwhile, the high temperature ~4000–6000 K facilitates the breakdown of the surrounding gas filled inside the chamber. The gas ionizes into electrons and ions and results in hot plasma formation between the electrodes. Stable plasma grows uniformly over the electrode surface corresponding to stable anode and cathode voltage. The collisions of ions and electrons in the plasma emit photons responsible for the glow in plasma. The electrons are ejected from cathode hit the anode at high velocity and sputter the carbon precursor filled at the centre of the anode.

The high temperature resulting from resistive heating results in sublimation of carbon precursor and converts them into carbon vapours. The carbon vapours are decomposed in carbon ions. The decomposition occurs due to high heat flux or thermal energy of the plasma. The carbon vapours aggregate to form viscous carbon clusters and drift towards the cathode, which is cooler as compared to anode. The carbon vapours undergo a phase change and get converted into liquid carbon. The temperature gradient at cathode and quenching effect of atmosphere solidifies and crystallizes the liquid carbon to form cylindrical deposits that grow steadily on cathode. The cathodic deposit is composed of a grey outer shell and a dark inner core. The grey deposit consists of the rolls of graphene sheets known as carbon nanotubes. The addition of hexagonal carbon atom clusters lead to the growth of nanotube. However, instability in plasma leads to capping of nanotubes. The diameter of the nanotubes is governed by the density of carbon vapours in the plasma. Variation in temperature gradients strongly affects the diameter distribution of CNTs produced and nanotubes are formed in bundles due to van derWaals interaction. In reported literature, mechanism of nanotube synthesis has been explained by few researchers [1–20] but the exact growth mechanism is still debatable due to different theories of nanotube growth in vapour phase [12], liquid phase [11], solid phase [13] and crystal phase [21]. Gamaly and Ebbesen [12] detailed the vapour phase growth of MWNTs and suggested that the carbon vapours condense and nucleate to form nanotubes. They proposed a model for the velocity distribution of carbon vapours and divided the carbon vapours in two groups depending upon their velocity distributions. One group of carbon vapours will have the isotropic (Maxwellian) velocity distribution. The other group of carbon particles has higher velocities than the first group which is due to the acceleration of carbon vapours between the electrodes. According to Gamaly and Ebbesen, the nanotube growth occurs in three steps seed formation, tube growth and termination. The seeds are formed as a result of the two velocity distributions. In the beginning, the carbon vapours possess Maxwellian distributions which result in nanoparticle formation. Upon increasing the current, the other group of directed carbon vapours results in open structures or seeds. Once the current reaches a stable value, the carbon ions flow perpendicular to the cathode surface resulting in the nanotube growth. Finally the nanotube growth is terminated due to instabilities in the plasma. A similar theory has also been validated by other researchers [22–27]. The formation of carbon nanotubes by the arc discharge method is the most accepted one. In this method, the nucleation and growth take place by the direct condensation of the vapor or the plasma phase. It has been suggested that during the synthesis of CNTs, two types of carbon particles accelerate between the cathode and the anode. One group of particles follows the Maxwellian velocity distribution, i.e., isotropic, and the other group of carbon particles accelerates in the gap between the anode and the cathode and has a higher velocity than the former. The process of carbon nanotubes formation is considered in three stages. In the first stage, the isotropic velocity distribution promotes the formation of carbon nanoparticles and these nanoparticles work as seeds for the growth of nanotubes. In the second stage, a stream of directed carbon ions flows in a direction perpendicular to the cathode surface, which promotes the rapid growth of tubes. Finally, instabilities in the arc discharge lead to the abrupt termination of the growth of nanotubes by the formation of caps.

2. Experimental Setup

In this section we prepared a indigenous Arc discharge setup for CNT syntheses we designed setup for mass production of CNT Synthesis of carbon nanotubes via the arc discharge system under the inert gas environment. The 3D model was developed via Solid Works 2017. The schematics of a typical arc discharge system are presented in Fig. 1 In our present system, the electric arc is generated between the two graphite

electrodes, of which one is the anode and the other is the cathode. Both the electrodes were mounted horizontally in a typical cylindrical quartz reaction chamber under an inert gas environment. An argon gas cylinder was used to provide an inert atmosphere. For the synthesis of CNTs, a DC power supply with a current range of 95–100 A under the potential difference of 15–20 V was used for several minutes. The electrode was brought into contact for generating the arcing plasma with a gap of 1–2 mm between the two electrodes. During the experimental run, argon gas continuously flowed through the reaction chamber. During the experiment, the arc current generated the plasma with very high temperatures ranging from 4000 K to 6000 K, leading to the evaporation of the anode. The generated carbon vapor then condenses inside the cathode. After the completion of the experimental run, the carbon soot deposited on the cathode and inside of the reaction chamber walls was collected and subjected to characterization. The main parts of the setup is also mention in the fig.1 these are cathode, anode, DC power supply, Argon Cylinder, Exit gas Trap, Quartz tube, pressure Gauge, Inert gas inlet, exhaust, and wire connection.

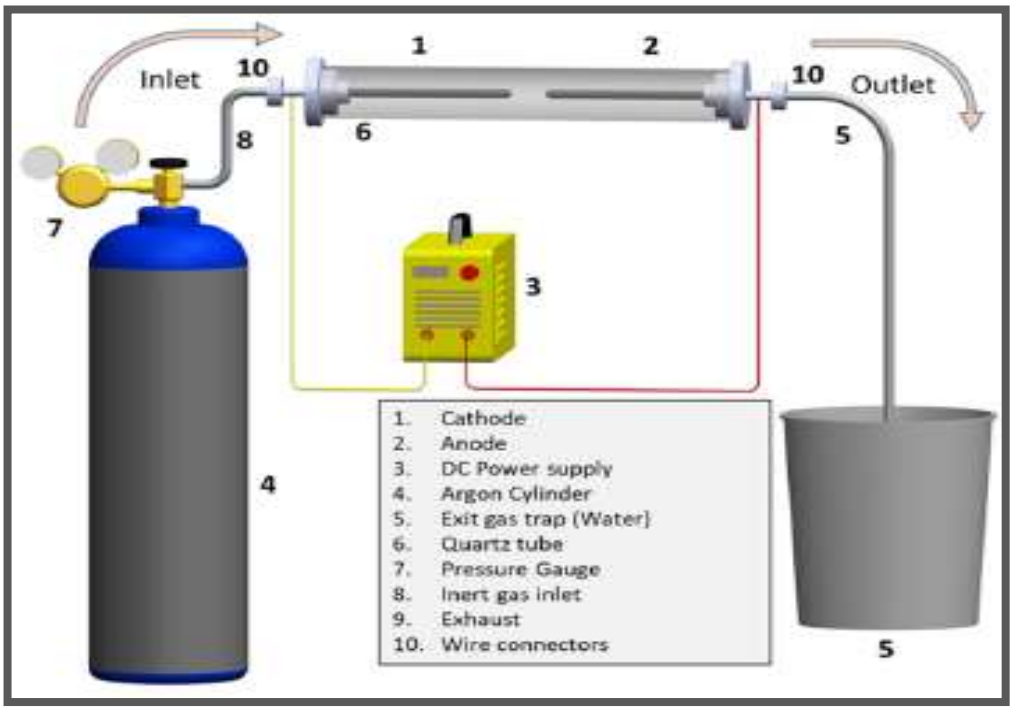

Fig. 1 Schematics of electric Arc discharge setup under inert gas (Ar) Environment

Fig.2 shows the actual picture of the system which is developed in the university lab the indigenous system is very simple in construction its main parts also described. The system has been completely installed and initial testing and calibration of electric arc discharge system in gaseous medium has been done and optimization of several synthesis parameters for qualitative growth of CNT is done and we found higher yield of better quality CNT as comparison to under water arc discharge setup.

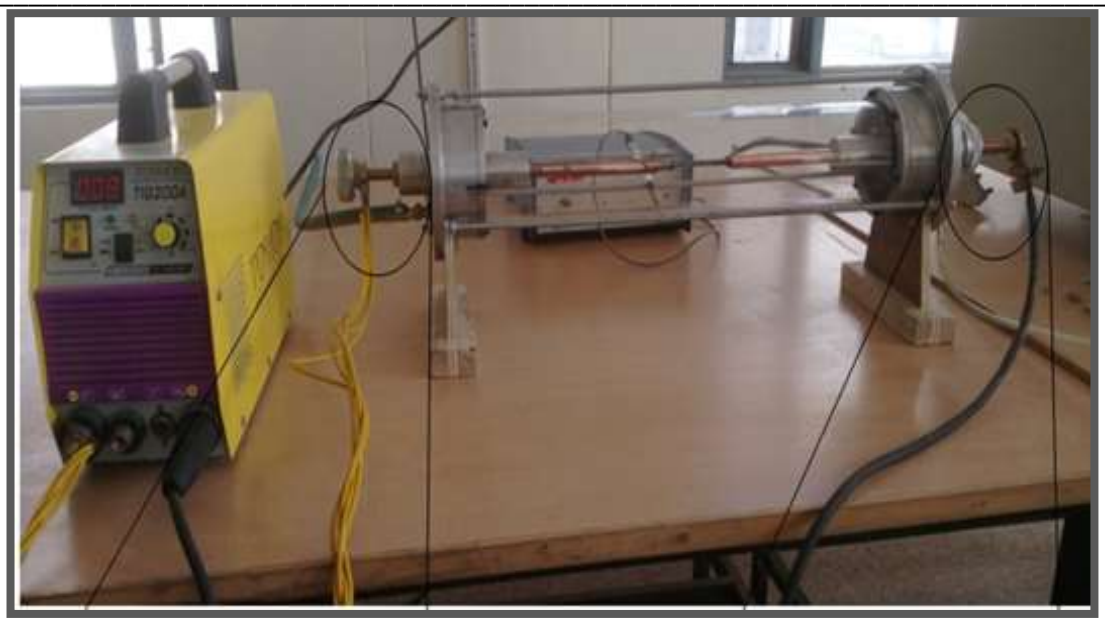

Fig. 2 Lab setup of electric Arc discharge setup under inert Gas Environment

3. Methodology

The methodology process involve following steps In first step we have used pure graphite rod which have 5mm diameter & 40 mm long length as a cathode. and similarly pure graphite rod which have 5mm diameter and 100mm long length as a anode and we doesn't did any type of doping then it has been found that the fine carbon shoot has been deposited at entire area inside the arcing tube as shown in Fig.3 which shows carbon shoot deposited on entire wall of tube. Fig 4 shows how a carbon shoot deposited at electrodes fig part (c) shows carbon shoot deposited at cathode side portion fig part(d) shows carbon shoot deposited at anode side portion and fig part (e) shows carbon shoot deposited at cathod.

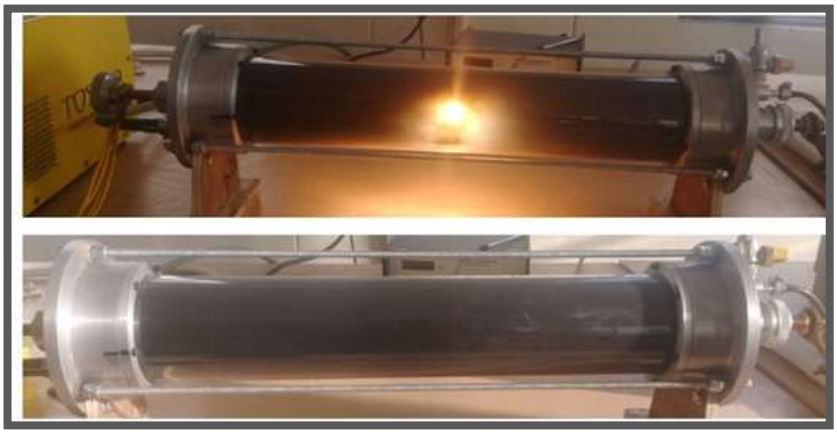

Fig. 3 Intensity of Arching Plasma when arching with pure graphite rod as anode

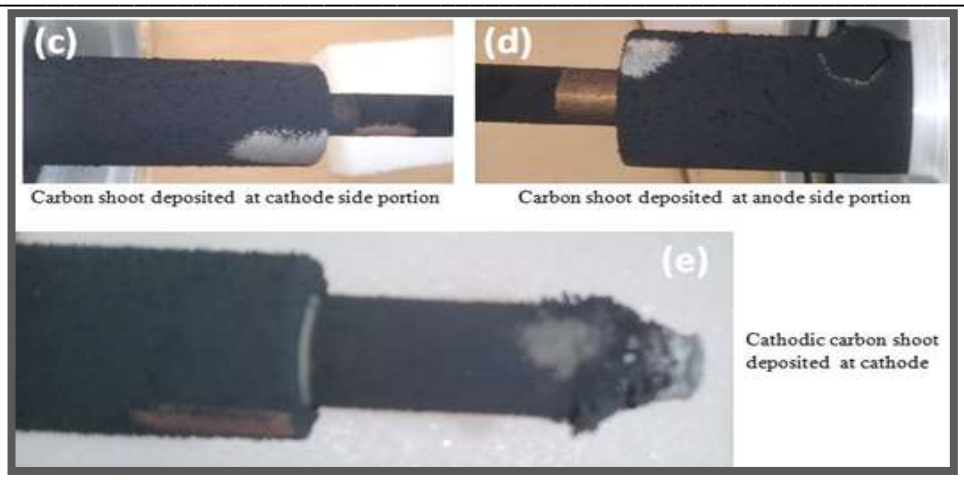

Fig. 4 Carbon shoot deposited on cathode & Anode.

In second step we have used pure graphite rod which have 5mm diameter & 40 mm long length as a cathode. and pure graphite as a anode but in this step we doped anode with Fe and Co nano powder that serve as a catalyst during CNT growth The mixture of Fe+Co nano powder was filled in graphite rod by mean of drilling a 50 mm deep hole at the top centre of anode rod and heat upto 500 ºC for 6 hr. the anode have 5mm diameter and 100mm length. It was observed that when using anode with catalyst doped graphitic rod then most of arcing product obtained in form of cathode shoot at the top of cathode and comparatively less carbon shoot has deposited in limited portion of tube near the arcing area as shown in fig.5

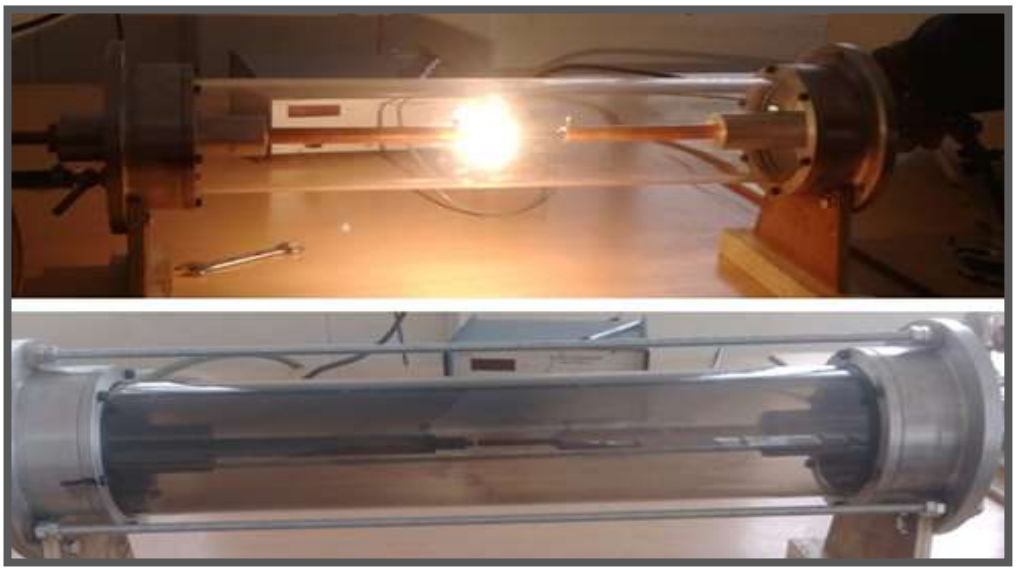

Fig.5 Intensity of Arching Plasma when arching with Doped graphite rod as anode

Fig.6 Cathodic shoot with respect to time interval

Fig 6 shows the deposition of carbon shoot in different- different time interval which shows the most of arcing product obtained in the form of cathode shoot means most of deposition take place at the top of cathode and if we compare it with step first it is found that less carbon shoot has deposit in limited portion of tube near arcing area. In fig we consider three conditions with respect to the time intervals of 2min 3min and 5min after starting the process.

4. Result and discussion

In this section of the experiment, we will discuss the characteristics analysis of yields found in the synthesis process. The analysis process includes structural analysis, spectroscopic analysis. and morphology analysis.

Structural Analysis It was used to investigate the crystallographic order, impurity content & flaws in synthetic materials. In this case, the XRD pattern is captured over 2 ranges from 0 to 80° at 0.5°/min. The sharp peak at $2\Theta = 26°$ corresponds to the (002) hexagonal phase of a highly crystalline carbon crystal system. The two wide peaks at $2\Theta = 43°$ and 54° relate to various carbon structures.

Spectroscopy Analysis For researching the chemical & electrical properties of carbon nanostructured materials, Raman spectroscopy is used. One of the essential characterisation techniques for carbon nanotubes, single-walled and multi-walled, and graphene and its composites. Ideal CNTs feature three peaks at 1350, 1591, and 2657 cm-1. The D band is produced by flaw and disorder components in CNTs breathing style of sp2-hybridization. The D band's strength is related to the CNT's defect count. The G band's second peak is created by the in-plane vibration of sp2 carbon atoms. The 2D band (formerly known as the G band) is an overture of the D band created by two phonons with opposite momentum interacting. The 2D band's location and form are sensitive to the thickness and number of layers of graphitic material, and in this situation, it shows tubular layered synthesis This section compares each combination's Raman spectroscopy to the ideal CNT Raman analysis.

Morphology Analysis A scanning electron microscope (SEM) examines the surface of a sample with a high-energy electron beam. Zeiss (20 kV) was used to characterise the morphology of the graphene-based nanostructured material in this study. Electrons interact with atoms in a sample to produce signals that reveal surface topography, composition, and other properties like electrical conductivity. Using an SEM instead of a light detector has various advantages. According to the SEM picture of CNTs synthesised by the

underwater arc discharge setup, the morphology of synthesis materials demonstrates that the as-produced materials are CNTs.

1. Structural Analysis

Fig. 7 shows the XRD analysis of Synthesized Product when pure Graphite used as a Anode it shows the curve is not smooth it means yeild found after synthysis is not pure some other form of carbon also presend in the product.

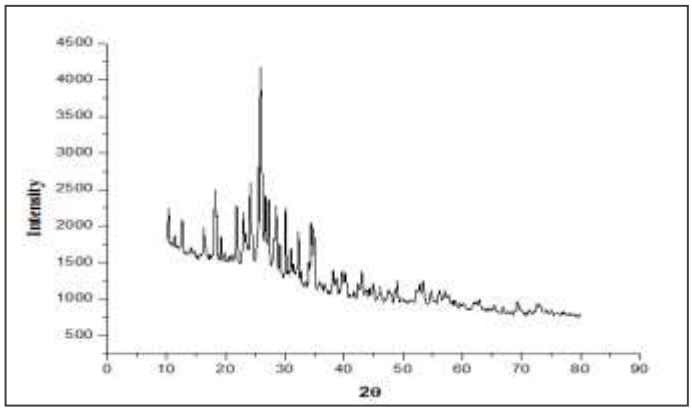

Fig. 7 XRD spectra of Synthesized Product when pure Graphite used as a Anode

Fig. 8 shows the XRD Spectra of Synthesized Product when doped Graphite used as a anode. For The doping we use mixture of Fe + Co in the ratio of 1:3 and found that amount of impurity is decreased.

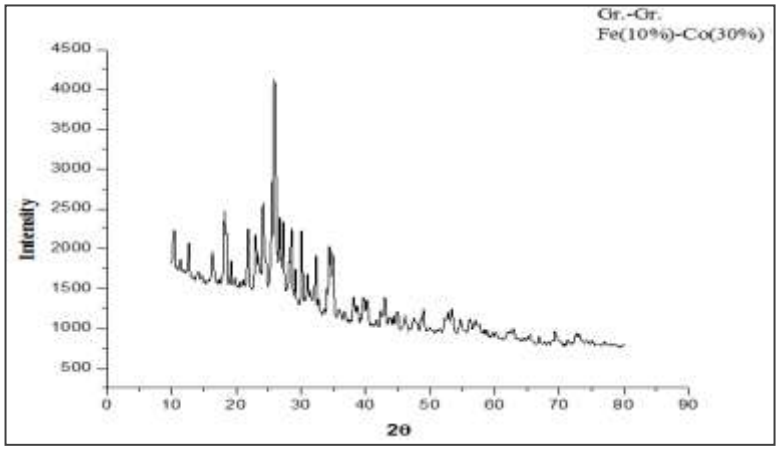

Fig. 8 XRD Spectra of Synthesized Product when doped Graphite used as a Anode

2. Spectroscopy Analysis

Fig 9 and fig 10 shows the Raman analysis for pure graphite anode combination and doped graphite anode combination which shows the after doping the quality and quantity of the yield is improved.

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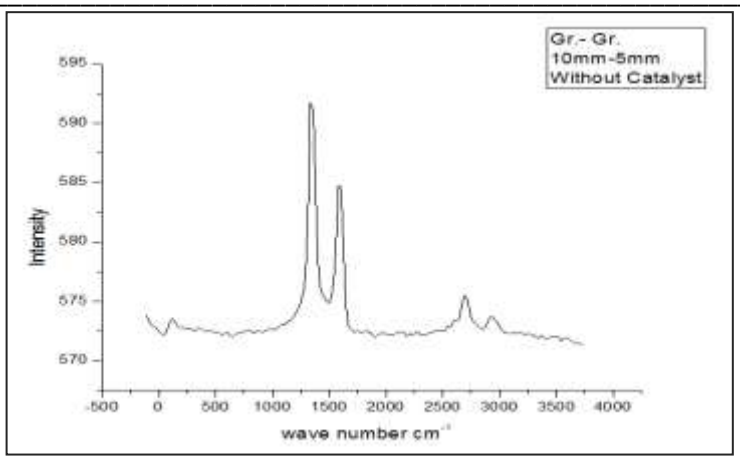

Fig. 9 Raman analysis of Synthesized Product when pure Graphite used as a Anode

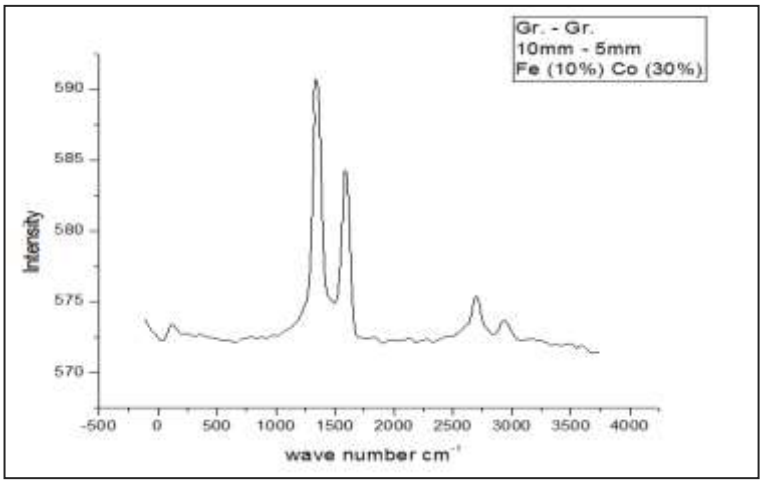

Fig. 10 Raman analysis of Synthesized Product when doped Graphite used as a Anode

3. Morphology Analysis

Fig. 11 and fig.12 shows the SEM analysis for pure graphite anode combination and doped graphite anode combination which validates the tubular morphology of the materials.

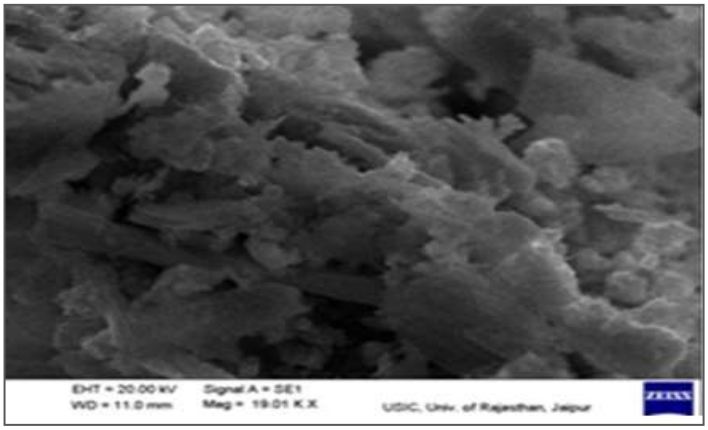

Fig. 11 SEM image of Synthesized Product when pure Graphite used as a Anode

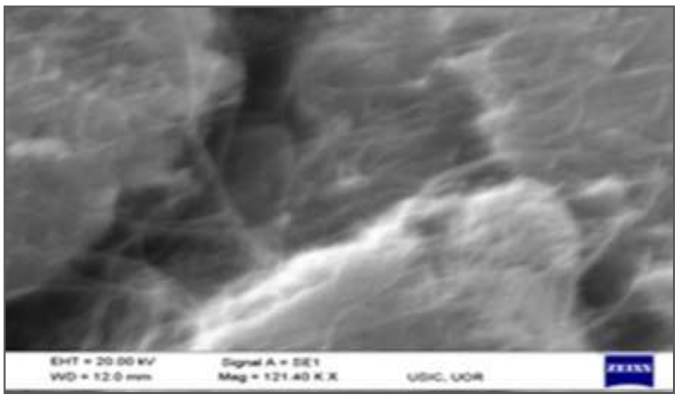

Fig. 12 SEM image when Fe + Co nano powder mixture doped

5. Conclusion

Indigenous systems for the bulk production of CNTs have been designed, developed, and assembled at the Renewal Energy Laboratory, Vivekananda Global University, Jaipur. The under Gas arc discharge system featured in a quartz tube with high current and low voltage. Role of Catalyst, material, described during CNT synthesis. The authenticity of the produced CNTs was verified using powder XRD, Raman spectroscopy, and SEM. Graphitized CNTs are visible in the Raman spectra of newly produced CNTs. SEM verifies the tubular shape of the materials produced here. Moreover, the produced CNTs do not need additional purification, allowing their usage in research or industrial applications. Indigenous Discharge mechanism for gram scale Growing CNTs is simple and saves energy.

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