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Der Chemica Sinica, 2012, 3(5):1058-1070

ISSN: 0976-8505
CODEN (USA) CSHIA5

# Synthesis of carbon nano material from different parts of maize using transition metal catalysts

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## ABSTRACT

*The waste parts of maize plant (dried stem, mature calyx attached to fruits and hair present on the cob), on pyrolysis using three different nano transition metal catalysts (Ni, Fe and Co) and different temperatures (600, 800 & 1000$^0$C) in inert atmosphere; produced different types of Carbon Nano Materials (CNM). The Chemical Vapour Deposition (CVD) technique was used for synthesis of carbon nano materials. The morphology of CNMs was examined by high resolution scanning electron-microscopy (HRSEM), Raman spectroscopy and XRD. When Stem was used as precursor 1000$^0$C was found to be the most suitable temperature for producing CNM; which in presence of Ni was like a porous plate and the pores were the source of producing Carbon Nano Beads (CNB). Co was not effective in producing CNM from stem. Calyx also responded better to higher temperature (1000$^0$C).* In presence of Ni it produced net work of coiled CNTs. Fe *was not effective in producing CNM from calyx. Only Ni could produce thin branched Carbon Nano Fibres (CNF) from hair at 1000$^0$C.* XRD pattern of CNTs and CNB confirmed its graphitic nature. Graphitic peaks were weak in CNF samples. Raman spectrum also confirmed graphitic nature of CNT and CNB. The CNTs also showed peaks designated to multi-walled carbon nanotubes.

**Keywords:** Maize stem, Maize calyx, Maize hair, CVD, Catalyst, Ni, Fe, Co, Taguchi optimization

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## INTRODUCTION

Chemical Vapor Deposition (CVD) is a popular technique of growing carbon nano materials (CNM) [1,2, 3]; because it can be used with the foremost convenience and utmost control. That is why it is used from engineering college laboratories to industrial research laboratories on equal footing.

Although CVD is a well-established deposition technique since as early as 1950s, with the advent of revolutionary nanotechnology research in the last decade, it has attracted enormous interest towards the formation of nanomaterials. Because of the relative ease for creating materials of a wide range of accurately controllable stoichiometric composition, CVD has been getting unprecedented success in different arena of modern technology. The fundamental of CVD process is to convert a precursor into vapour form and then allow it to again transform into solid. In a nutshell, a mixture of gases passing over a hot surface undergoes chemical reactions which lead to a solid deposit on the surface.

The aim of this work is to use natural carbon resources instead of depleting fossil fuel derived materials and study the significance of various CVD parameters; in particular catalysts; for the synthesis of CNMs. Not only the type but the size of catalyst has also been found to impact the synthesis of carbon nano materials.

The precursor selected for the present work were three different parts of maize (*Zea maize* ) plant i.e. dried stem after harvest, mature brownish calyx and hairs present on the mature cob (elongated stigma). These parts are non-edible waste material. An initial elemental analysis of these parts showed that it contains comparatively higher amount of carbon (Table – 1), hence, can be a good source of carbon.

**Table – 1 Carbon, hydrogen and nitrogen content of different parts of maize plant**

| Parts of Maize plant | Carbon | Nitrogen | Hydrogen |
|---|---|---|---|
| Hair | 40.753 | 12.672 | 4.977 |
| Stem | 41.826 | 13.337 | 4.975 |
| Calyx | 41.161 | 14.249 | 5.702 |

## MATERIALS AND METHODS

***Precursors-*** Maize plants were collected from the fields near Mumbai farms. The parts used as precursor were (i) dried stem of mature plant after harvest (ii) Dry calyx taken from the mature cob of the corn and (iii) hair bunch that grows along with maize cob (Figure – 1). All the three precursors were dried in the lab at $40^0$C temperature in an oven to remove traces of moisture.

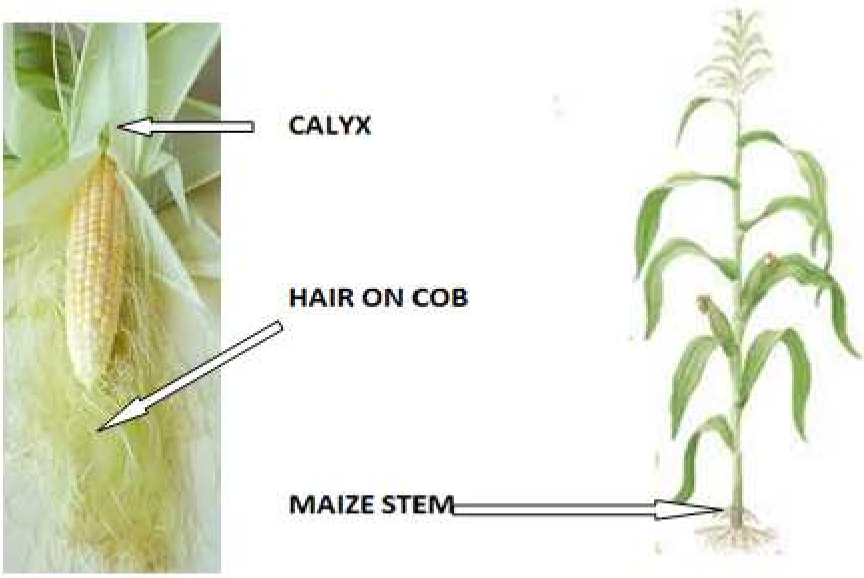



**Figure 1 – Different parts of a maize plant used for synthesizing CNM**

***Nano Carbon Synthesis Procedure*** - Chemical deposition method was followed for the pyrolytic reduction of hydrocarbons present in precursors into the nano carbon. CVD set up used was the same as described earlier by Sharon and Sharon (2006) [4].

CVD method was followed for the pyrolytic reduction of hydrocarbons present in precursors into the nano carbon. All the three precursors (i.e. stem, calyx and fruit hair) were subjected to three different variables of following parameters during CVD process viz. transition metal catalysts (Ni, Co, and Fe), temperature ($600^0$c, $800^0$c and $1000^0$c) type of carrier gases ($H_2$,$N_2$ and Ar) and duration of pyrolysis was fixed to 2 hours.

The schematic diagram of chemical vapour deposition set up is given in the figure – 3 Precursor was placed in a boat along with catalyst and the boat was inserted in the center of the pyrolyzing furnace. After flushing the quartz tube with a carrier gas i.e. argon, hydrogen or nitrogen to make the reactor oxygen free. The furnace was heated to desired temperatures (600, 800 or $1000^0$C) and kept at that temperature for 2 hrs for completion of precursor to CNM conversion process. Heating was then switched off and furnace was allowed to cool to the room temperature. The carbon soot was collected from the furnace and purified by acid treatment to remove traces of catalyst, amorphous carbon and any plant residue. Yield of carbon was recorded prior to as well as after purification.

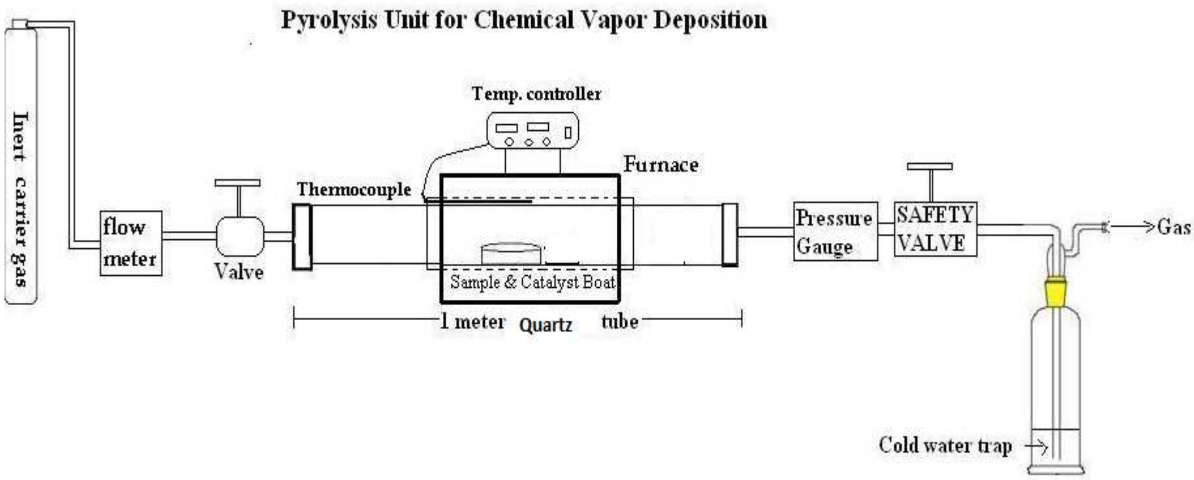



**Figure – 2: Schematic diagram of CVD set up used for pyrolysis of waste plant parts of Maize**

***Parameters considered for CVD –*** As mentioned above all the three precursors were subjected to three different variables of following parameters during CVD process

**1. Carrier Gases –** which helps to maintain the inert atmosphere required in the pyrolyzing furnace and also helps to carry the gases produced in the pyrolyzing furnace during the preparation of CNMs. Hydrogen, nitrogen and argon are the three gases selected as carrier gases for the present work.

**2. Pyrolyzing Temperature -** Higher temperature is preferred for the pyrolysis of solid precursors rich in hydrocarbon; hence, $600^0$C, $800^0$C and $1000^0$C were selected for CVD process. At higher temperature ash formation is reduced and more vaporization of carbon takes place.

**3. Catalysts -** From the literature survey, it was observed that the transition elements give good results in the preparation of CNMs using plant derived sources as precursors. Such CNM provide a large surface area for the adsorption [5]. Hence, the transition metals cobalt, nickel and iron were selected as catalysts for the production of CNMs in the present work. From the salts of all these three metals [$Ni(NO_3)_2$, Co $(NO_3)_2$ and $Fe(NO_3)_3$ **]** nano metals catalysts were prepared using Urea Decomposition Method. Following reaction took place during the oxidation & reduction processes:

For Ni

$Ni\ (NO_3)_2\ 6\ H_2O + (NH_3)_2.CO \rightarrow$ Ni-Oxide + 4 $CO_2 + NH_3$

$NiO + H_2 \rightarrow$ Ni- nano particles + $H_2O$

For Co

$Co\ (NO_3)_2.6\ H_2O + (NH_3)_2.CO \rightarrow$ Co-Oxide + 4 $CO_2 + NH_3$

Co-oxide + $H_2 \rightarrow$ Co-nano particles + $H_2O$

For Fe

$Fe(NO_3)_3.6\ H_2O + (NH_3)_2.CO \rightarrow$ Fe-Oxide + 4 $CO_2 + NH_3$

Fe-oxide + $H_2 \rightarrow$ Fe- nano particles + $H_2O$

**CNM Preparation Using Taguchi Optimization Method**

The Taguchi optimization method [6] involves reducing the variation in a process through robust design of experiments. The overall object of the method is to produce high quality product at low cost to the manufacturer. However, it has found application in research as it reduces the number of experiments to be carried out. The experimental design proposed by Taguchi involves using orthogonal array to organize the parameters affecting the process and the levels at which they should vary. Instead of having to test all possible combinations, the method tests pairs of combinations that allows for the collection of the necessary data to determine which factor most affect product quality with minimum amount of experimentation, thus saving time and resources.

Including precursors there were four parameters, each having three variables. Consideration of permutation combinations of all the parameters would have involved several pyrolysis experiments. To reduce the number of experiments Taguchi Method for Optimization of parameters was followed. For such combination the standard pattern of ***L9 Orthogonal array*** was chosen and is presented in table – 2 and 3.

**Table- 2: Four Selected parameters and their levels used for synthesis of CNM by CVD process**

| Parameters | | Levels | | |
|---|---|---|---|---|
| | | **1** | **2** | **3** |
| **P1** | **Gases** | **Argon** | **Nitrogen** | **Hydrogen** |
| **P2** | **Temperatures** | $600^0$C | $800^0$C | $1000^0$C |
| **P3** | **Precursors** | Maize cob hair | Maize calyx | Maize Stem |
| **P4** | **Catalyst** | Cobalt | Nickel | Iron |

In the orthogonal array (Table – 3) the columns are mutually orthogonal that is for any pair of columns, all the combinations of factor, levels occur at an equal number of times. Here there are four parameters P1, P2, P3 and P4 each at three levels. This is called an L9 design with the 9 indicating the nine rows, configurations or prototypes to be test.

Thus L9 means that nine experiments are to be carried out to study four variables at three levels. This design reduces 81 configurations to nine experimental evaluations.

**Table – 3: Orthogonal Array of L9 Experiments**

| Levels | Parameters | | | |
|---|---|---|---|---|
| | P1 | P2 | P3 | P4 |
| L1 | 1 | 1 | 1 | 1 |
| L2 | 1 | 2 | 2 | 2 |
| L3 | 1 | 3 | 3 | 3 |
| L4 | 2 | 1 | 2 | 3 |
| L5 | 2 | 2 | 3 | 1 |
| L6 | 2 | 3 | 1 | 2 |
| L7 | 3 | 1 | 3 | 2 |
| L8 | 3 | 2 | 1 | 3 |
| L9 | 3 | 3 | 2 | 1 |

***Characterization of nano metal catalyst***, prepared by urea decomposition method, was done by HRSEM.

***Characterization of Carbon:*** The morphological observations of as-synthesized and purified carbon nanomaterials were carried out by Scanning Electronic Microscope (SEM). SEM was conducted using a Hitachi (S-4700) SEM by placing the as-prepared samples on conductive carbon tape.

XRD of carbon nanomaterials was performed with a powder X-ray diffractometer with CuKα source to calculate the crystallographic parameters.

Raman spectra were measured in a backscattering geometry at room temperature using Ar ion laser (488nm).

## RESULTS AND DISCUSSION

### *Morphology of Catalysts*

As it can be seen from figure – 3a, **Fe** nanoparticles were developing into spherical structure from the plate like flat forms. The size of spherical or bead like structure varied from 50 to >100nm.

**Ni** nano particles also exhibited (Figure 3c) spherical beaded structures originating from plate like flat forms. Size of Ni nano particles also varied from 50 to > 100nm

**Co** nano particles had needle like structure (Figure 3b); on an average they were approximately 500nm long with pointed ends. However presence of some flat plate like structures could also be seen

### *Yield of CNM*

For analyzing the material that would give best result, "larger the better" condition was selected. Using the output of experiments, (i.e., the magnitude of absorption) S/N ratio has been computed by the equations (1).This ratio determines the dominance of a particular parameter for the formation of the product.

Taking "Larger –the- better" option, S/N ration is calculated from the following expression, ratio.

$$S/N = -10\ Log\ (1/n) \sum 1/y_i^{\ 2} \qquad \text{.......................................[1]}$$

Where, $y_i$ is mean of the yield of the product and n, is the number of repetitions of each experiment.

***S/N ratio and sum of the S/N ratio*** for the individual parameter which is required to determine the effect of each parameter level (mi).

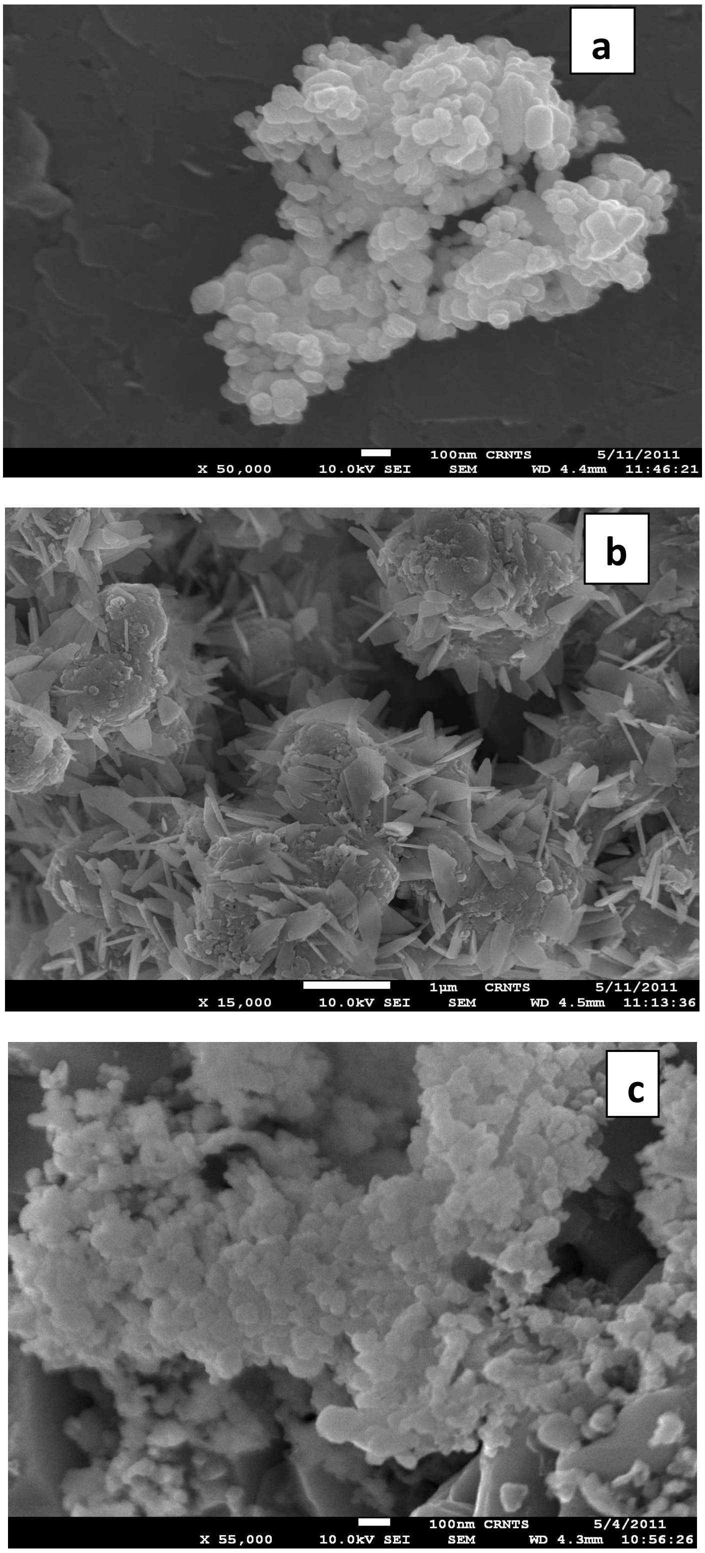



**Figure – 3: SEM of Metal Catalysts (a) Fe (b) Co and (c) Ni; prepared by urea decomposition method**

***Effect of Each Parameter on the Yield of CNM***

To determine the effect of each parameter level (mi), average value of S/N ratios are calculated for each parameters using analysis of mean (ANOM). For this calculation, the S/N ratios of each experiment with corresponding parameter levels are employed.

$$m_i = \left( 1/N_i \right) \sum S/N$$

Where *Ni* is the number of experiments conducted with the same parameter levels. Two types of average value of S/N ratio are calculated.

The parameters effects, i.e. the contribution of each experimental parameter to the quality characteristic, are calculated by the analysis of variance (ANOVA). Finally the factor of effects (FoE) of various experimental parameters is calculated using the equation,

$$FoE = \frac{SoS}{DoF \times \sum (SoS / DoF)} \text{-}$$

The results obtained are as discussed below:

The effect of different parameters like carrier gas (P1), temperature (P2), precursors (P3) and catalyst (P4) on the performance characteristics in a condensed set of experiments is shown in the following tables.Two sets of Taguchi Orthogonal array are prepared.

**Table 4: Yield of CNM from 1 g precursor pyrolyzed for 2 hrs**

| ExpNo | P1 | P2°C | P3 | P4 | Yield of Impure CNM (g) | Purified CNM (g) | %pure Carbon Obtained |
|---|---|---|---|---|---|---|---|
| **L1** | Ar | 600 | Hair | Co | 0.977 | 0.255 | 26 |
| **L2** | Ar | 800 | Calyx | Ni | 0.802 | 0.240 | 30 |
| **L3** | Ar | 1000 | Stem | Fe | 0.364 | 0.147 | 40 |
| **L4** | $N_2$ | 600 | Calyx | Ni | 0.929 | 0.032 | 3 |
| **L5** | $N_2$ | 800 | Stem | Fe | 0.328 | 0.040 | 13 |
| **L6** | $N_2$ | 1000 | Hair | Co | 0.970 | 0.037 | 4 |
| **L7** | $H_2$ | 600 | Hair | Fe | 0.785 | 0.084 | 11 |
| **L8** | $H_2$ | 800 | Calyx | Co | 0.877 | 0.148 | 17 |
| **L9** | $H_2$ | 1000 | Stem | Ni | 0.803 | 0.127 | 17 |

From the table – 4, it is observed that level-3 gives maximum and level- 4 gives minimum yield of pure carbon. So it can be said that the stem yields more carbon when pyrolyzed at highest tried temperature ($1000^0$C) in presence of Ar, may be because at this temperature most of the residual chemicals present in the plant material got evaporated.

To know the detailed impact of each parameter on yield, signal to noise ratio (S/N ratio) was calculated using the formula mentioned above, which is presented in table – 5 and figure - 4

A histogram (Figure - 4) of S/N Ratio based on data from table – 5 shows the deviation on x-axis and parameter levels on y-axis. The maximum S/N Ratio is for level- 2 and the minimum is for level-5.There was two negative values for level-3 and level-5. The rest of the values of S/N ratio were positive

**Table 5 - S/N Ratio, as calculated using Taguchi methodology**

| Exp. No. | Experimental Conditions | | | | S/N Ratio |
|---|---|---|---|---|---|
| | P1 | P2 | P3 | P4 | |
| **L1** | Ar | $600^0$C | Hair | Co | 17.187 |
| **L2** | Ar | $800^0$C | Calyx | Ni | 18.906 |
| **L3** | Ar | $1000^0$C | Stem | Fe | -5.769 |
| **L4** | $N_2$ | $600^0$C | Calyx | Ni | 17.629 |
| **L5** | $N_2$ | $800^0$C | Stem | Fe | -6.666 |
| **L6** | $N_2$ | $1000^0$C | Hair | Co | 17.254 |
| **L7** | $H_2$ | $600^0$C | Hair | Fe | 19.092 |
| **L8** | $H_2$ | $800^0$C | Calyx | Co | 18.300 |
| **L9** | $H_2$ | $1000^0$C | Stem | Ni | 18.895 |

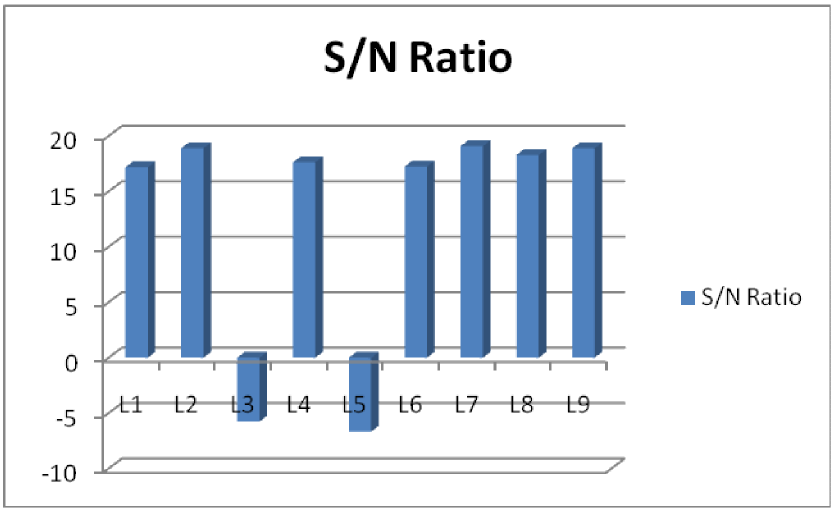



**Figure – 4: Deviation of S/N ratio of each parameter**

Impact of each parameter i.e. factor effect was calculated (Table – 6) it was observed that for 2 hrs pyrolysis duration, precursor act as the best parameter for synthesis of CNM. Catalyst is the next to have its impact on CNM preparation whereas the other two parameters (carrier gas and temperature) do not have much effect much on CNM synthesis.

**Table – 6: Details of Calculations for Factor Effect**

| | **Factors** | **Average by factor levels (mi)** | | | **DoF** | **SoS** | **SoD/DoF** | **∑ SoD/DoF** | **Factor Effect (F) = SoD/DoF x ∑(SoD/DoF)** | **% Factor Effect** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | | | | | | |
| 1 | **Precursors** | 17.844 | 18.278 | 2.153 | 2 | 168.80 | 84.398 | 215.432 | 0.3917 | 39.17 |
| 2 | **Carrier gas** | 10.108 | 9.405 | 18.762 | 2 | 54.313 | 27.156 | 215.432 | 0.1260 | 12.60 |
| 3 | **Temperature** | 17.969 | 10.179 | 10.127 | 2 | 40.727 | 20.363 | 215.432 | 0.0945 | 09.45 |
| 4 | **Catalyst** | 17.580 | 18.477 | 2.219 | 2 | 167.03 | 83.515 | 215.432 | 0.3876 | 38.76 |

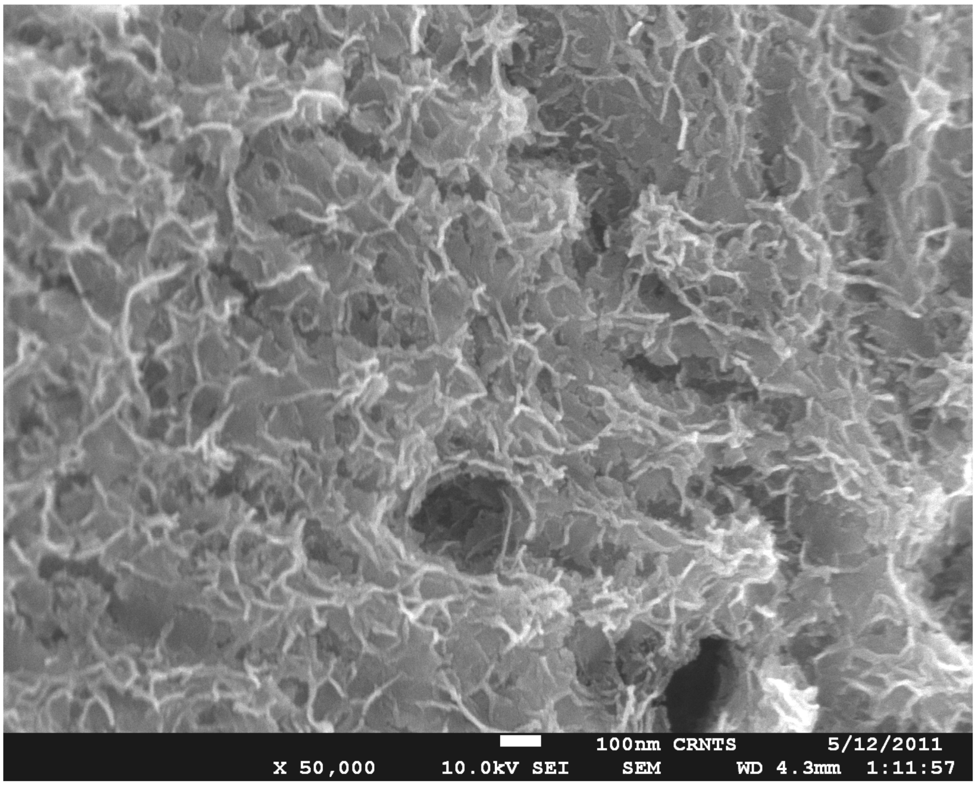



**Fig.-5: HRSEM of CNM synthesized from Maize Hair in presence of hydrogen & Ni at 1000$^0$C**

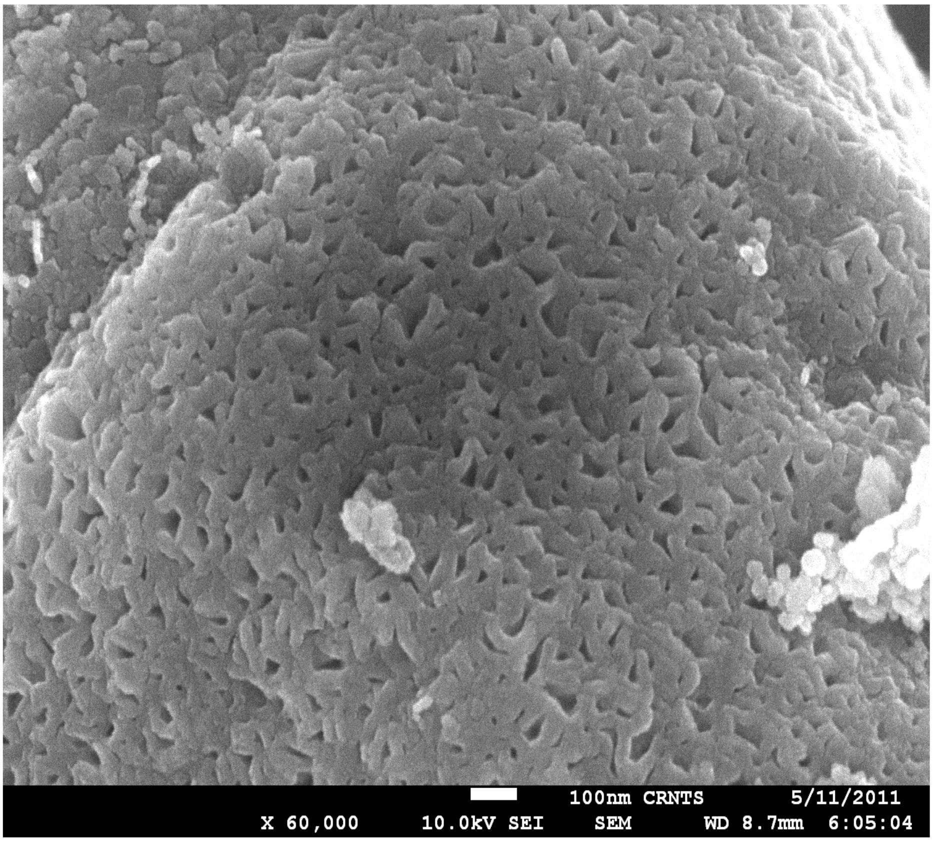



**Fig.-6: HRSEM of CNM synthesized from Maize Calyx in presence of Ni &Ar at 800$^0$C showing a network of tubules having rather thick diameter**

Apart from yield the interest was also focused on assessing whether the products were nano carbon or not, and whether the catalyst has any role in converting precursor into graphitic nano carbon structures.

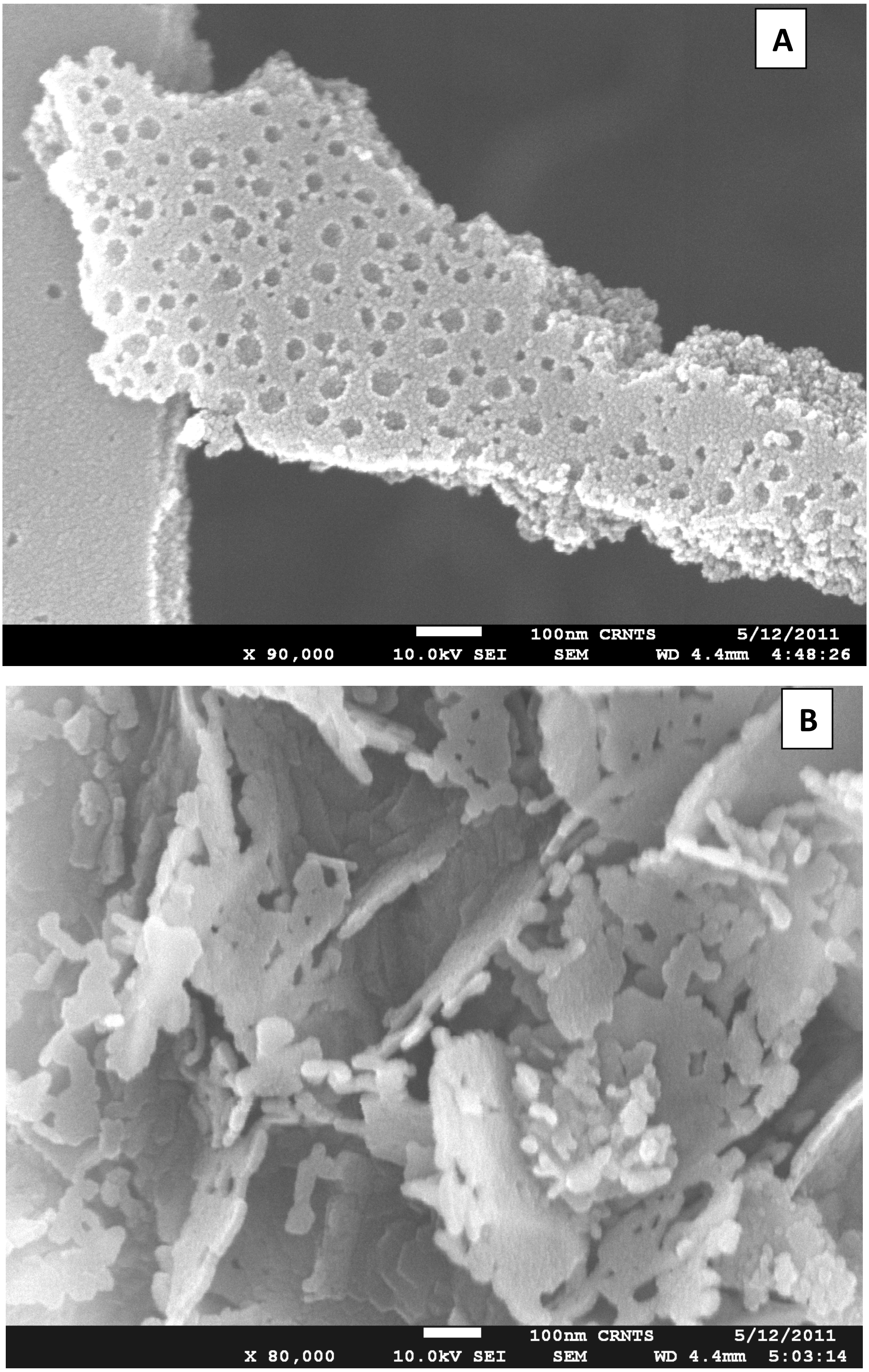
***SEM Analysis of CNM synthesized from Different parts of Maize***

Only those SEM analysis are presented below that showed reproducible structure at least twice.

Maize **Hair** in presence of hydrogen at 1000$^0$C and with Ni as carrier gas, formed very thin thread like branched nano fibres (Figure - 5).

When **calyx** of maize was pyrolised at 800$^0$C, in presence of as Ni catalyst and Ar as carrier gas a network of tubules having rather thick diameter were formed (Figure -6).

As it can be seen from figure 7 **stem** as precursor, on pyrolysis produced porous plates having on an average about 50 nm diameter holes. Figure b very clearly shows that the holes are due to carbon nano beads originating from the. Moreover the size of beads matches with that of the holes. Some very small beads can be seen on the outer diameter of the holes as well as on the surface of the plates too (Figure – 9)


A
100nm CRNTS 5/12/2011
X 90,000 10.0kV SEI SEM WD 4.4mm 4:48:26
B
100nm CRNTS 5/12/2011
X 80,000 10.0kV SEI SEM WD 4.4mm 5:03:14

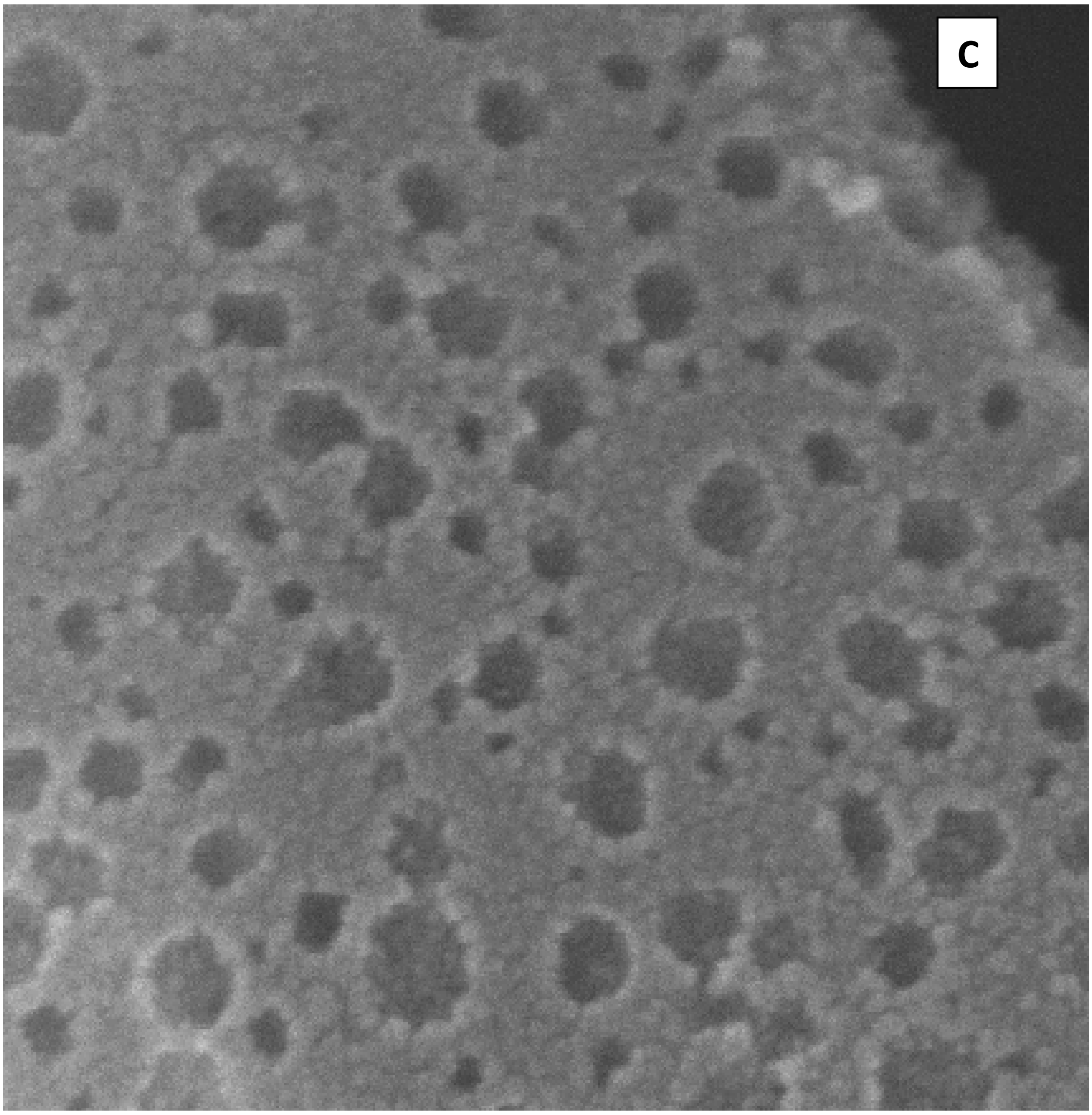
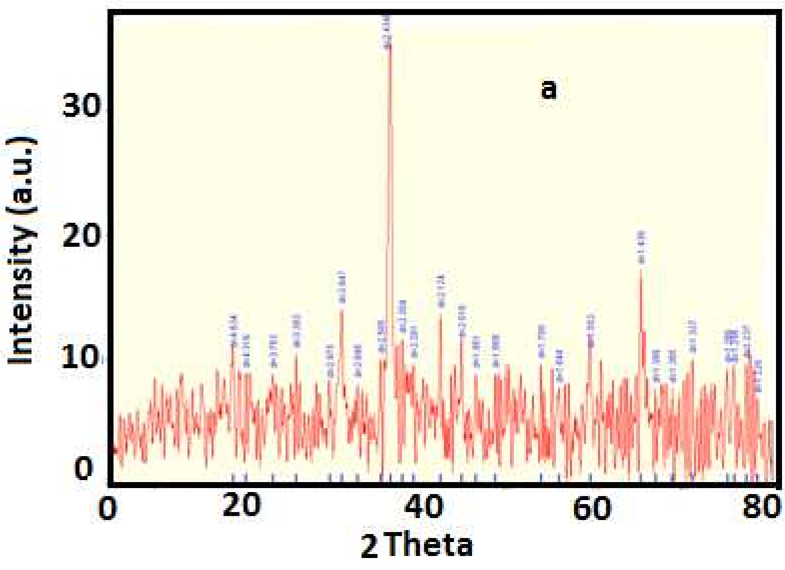
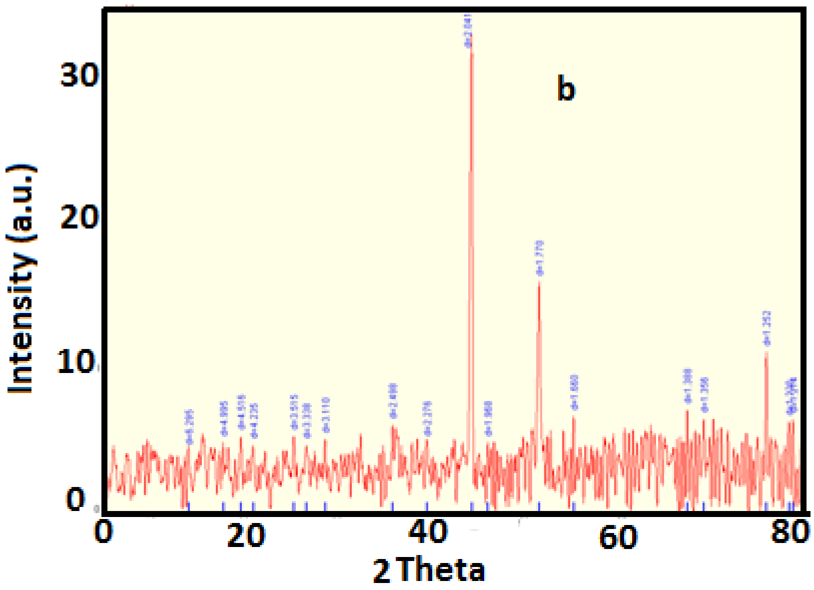



**Fig.-7: SEM of CNM synthesized from Maize Stem in presence of Ni &$H_2$ at $1000^0$C showing a (A) Porous plates of Carbon (B) Porous plates with bead like structure and (C) part of enlarged CNM plate taken from A, showing spherical bead like structures all over the plate and surrounding the holes**





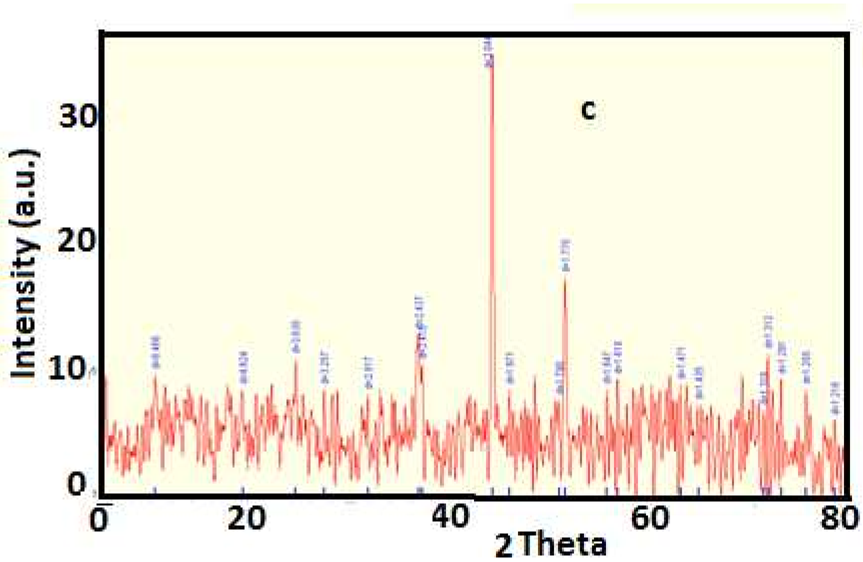




**Figure-10: XRD pattern of (a) CNF synthesized from Maize Hair (b) CNT synthesized from Maize calyx and (c) CNB synthesized from Maize stem**

**XRD Analysis of CNM**

XRD pattern of carbon nano fibers (from maize hair), carbon nano tubules (from maize calyx) and carbon nano beads (from maize stem) were recorded (Fig. 10 a,b,c). XRD analysis of CNT and CNB show a diffraction peak at $26^0$ {002}, which according to Garcia-Gutierrez [7] is designated to graphitic carbon. Moreover, peak at $44^o$ is also seen in all three graphs that is known to be associated with carbon {111}. A small peak present at $78^o$ of XRD of castor oil depicts the presence of the Silica, which could be due to the boat in which the catalyst was placed. However, the graphitic peaks are not very prominent in CNF samples

**Raman spectroscopic analysis**

Raman spectroscopic analysis was done only for CNT & CNB as they showed graphitic nature. Both of them show D band as well as G band thus confirming its graphitic nature (Fig 7). Raman spectroscopy is used to differentiate between graphite, multi walled and single walled carbon nanotubes and layers. The Raman spectrum of CNT sample (Figure – 11a) shows two typical peaks of MWCNT one at around 1562 $cm^{-1}$ and the other around 1318 $cm^{-1}$; which corresponds to the typical Raman peaks of graphitic carbon and defects in graphitic carbon respectively. The peak at 1562 $cm^{-1}$ is attributed to the Raman active $E_{2g}$ in plane vibrational mode and is related to the vibration of $sp^2$ bonded carbon atoms in a two dimensional hexagonal lattice. The peak at 1318 $cm^{-1}$ is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite. In

CNBs obtained from maize stem, the intensity of D–band peak is weaker than that of G–band peak, which originates from the in-plane shows less defects i.e. more graphitic carbon and less disorder of the product thus preventing the layer from extending [8]

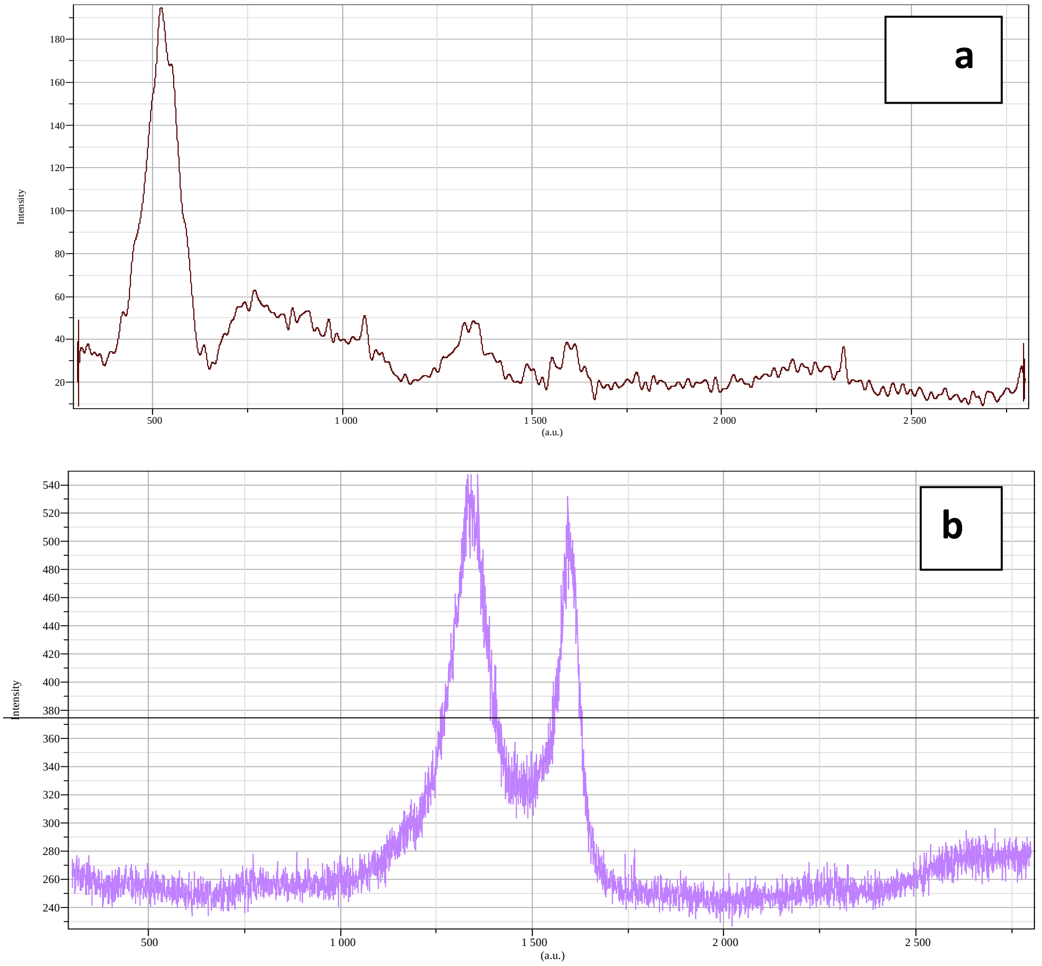



**Figure 11 – Raman Spectrum of (a) CNTs synthesized from Maize Hair and (b) CNBs synthesized from Maize Stem**

## CONCLUSION

Pyrolysis of waste parts of maize plant (dried stem, mature calyx attached to fruits and hair present on the cob), have been carried out under Ar, N2 and H2 gas at three temperatures (600oC, 800oC and 1000oC). Effect of catalyst on the production of carbon nanomaterials has been studied. Carbon materials have been characterised by SEM, XRD and Raman. Pyrolysis of Stem at $1000^0$C under Ni catalyst produced carbon nanomaterials. Pyrolysis of Calyx at $1000^0$C in presence of Ni it produced coiled CNTs. Ni could produce thin branched Carbon Nano Fibres (CNF) from Pyrolysis of hair at $1000^0$C with Ni catalyst pproduced carbon nanofiber. Other catalyst Fe and Co did not give satisfactory products. Taguchi Optimization methodology was used to establish the best parameters for the chemical vapour deposition to get the desired products.

**Acknowledgements**
Authors wish to acknowledge the support rendered by N.S.N. Research Centre for Nanotechnology & Bionanotechnology, Ambernath (W) for their support.

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