



# Growth of High Grade SWCNTs from Gr (a) Grass for Nano Drug Delivery System - A New Modified Feasibility Study

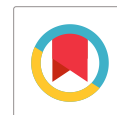
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## ABSTRACT

As a eco-friendly green carbon product liable to fuse inside the human body, biotechnologists and pathologists suggested and put forth a strong message that CNTs may be used as a nano capsule which carries drug towards cancer treatment. Modified AC method – VSA methodology (with KRS or NTFDS theory) was novelly adopted in this present work for the preparation of CNTs from natural organics i.e., Gr (a) grass towards the possibility of application to nano drug delivery system.. Structural, Compositional, Surface Morphological and Nano structural Characterizations were carried out on harvested products. The effects of optimizations parameters like pH of the various dipping solutions (acidic, basic and neutral), volume of dipping solutions, various types and parts of the materials, various dipping timings, number of annealing and dipping, various annealing temperature, various time of annealing and various dipping solution temperatures on structural, compositional, surface morphological, nano-structural characterizations of materials and on high grade SWCNTs growth with high yield were studied intensively. Inferences from characterizations were derived and graphically emphasized. Correlation studies between these characterization inferences (such as grain size, purity) and above optimization parameters were carried out with a high light on yield of high grade SWCNTs. Beyond all of these, we have carried out a new feasibility study at first time, which comprises the possible usage of precursor organic carbon sources for high grade SWCNTs with high yield via a low cost technique and methodology as value in commercial efforts.

**Keywords:** Gr (a) grass; HRTEM; Modified AC method; Nano drug delivery system; Natural organics;

## 1. INTRODUCTION

CNTs attract the scientific world due to their very peculiar physical and chemical properties. The present work made a break through at first time via plays an alternative method to conventional, traditional methods such as arc discharge, laser ablation, metal catalysts, pyrolysis and varieties of CVD methods and also removes the usage of synthetic chemicals as precursor materials. The present work showed that SWCNTs obtained by open air annealing and cooling of Gr (a) grass. The characterizations adopted to reveal the output products were standard and previously utilized by nanotechnology scientists and researchers throughout the world (Clark and Lyons, 1962; Newbury and Williams, 2000; Ge and Sattler, 1994; Zhang and Lieber, 1993; Zhenhui Kang *et al.* 2005; Vamvakaki and Chanlotakls, 2006; Withey *et al.* 2006; Gouveia-Caridade and Brett, 2008; Patolsky, 2004; Li and Wang, 2005; Iijima, 1991; Iijima and Ichihashi, 1993; Ajayan and Ebbesen, 1997; Ajayan and Iijima, 1993; Kyotani *et al.* 1996; Rao *et al.* 1997; Degani and Heller, 1987; Anto and Sayre *et al.* 1962; Chik and Xu, 2004; Masuda and Fukuda, 1995; Masuda *et al.* 1997; Li *et al.* 1998; Jessensky *et al.* 1998; Crouse *et al.* 2000; Liang *et al.* 2001; 2005; Wang and

Han, 2003; Yuan *et al.* 2004; Zhao *et al.* 2007; Hou *et al.* 2005). The novel modified AC method (Zhenhui Kang *et al.* 2005) – VSA methodology (with KRS or NTFDS theory) was adopted in this present work for the preparation of CNTs from natural organics: Gr (a) grass. The entire steps involved in the synthesis of SWCNTs from Gr (a) are:

1. Precursor materials selection with cleaning
2. Annealing
3. Sudden cooling,
4. Interaction between red hot natural organic carbon resource materials and Dipping solutions (DS) [including Nano Thermo Fluid Dynamics (NTFDS) and Nano-drilling process]
5. Harvesting of output products and dried for characterizations were briefly explained.

## 2. EXPERIMENTAL DETAILS

Gr (a) grass as a natural organic precursor material collected from nature, cleaned in water and dried in open air. The material was used without further

purification. Then the material was open air annealed (up to red hot) in a muffle furnace at various temperatures viz., 600 °C and 800 °C for various time of heating viz., 1 minute to 5 minutes. After that they were immediately dipped into various types of solutions viz., Sodium hydroxide (NaOH), Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), Nitric Acid (HNO<sub>3</sub>), Sulphuric Acid (H<sub>2</sub>SO<sub>4</sub>), Hydrochloric Acid (HCl), Mineral Water (MW), Salt Water (SW), Double Distilled Water (D2W), Ice Water (Ice W), Hot Water (HW), Pure Water (PW), Ice water mixed double distilled water (IceW+D2W) and Hot water mixed double distilled water (HW+D2W) solution for various solution temperature ranging from 0 °C to 100 °C, various time of dipping viz., 30 seconds, 45 seconds, 60 seconds, 75 seconds, 90 seconds and 120 seconds. The final samples were dried in open air at room temperature for 5 hours and then packed for characterization with mentioning synthesis conditions.

The above process was optimized with 11 Physical parameters viz.

1. Nature (pH) of the dipping solutions (acidic, basic and neutral)
2. Volume of Dipping Solution ranges from 0.5 ml, 1.0 ml, 1.5 ml, 2.0 ml, 2.5 ml
3. Various types of materials: fibrous conventional: varieties of plants, trees: Gr (a) grass
4. Various Parts of the materials: leaves
5. Various Dipping solutions: Sodium hydroxide (NaOH), Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), Nitric Acid (HNO<sub>3</sub>), Sulphuric Acid (H<sub>2</sub>SO<sub>4</sub>), Hydrochloric Acid (HCl), Mineral Water (MW), Salt Water (SW), Double Distilled Water (D2W), Ice Water (Ice W), Hot Water (HW), Pure Water (PW), Ice water mixed double distilled water (IceW+D2W) and Hot water mixed double distilled water (HW+D2W)
6. Various Dipping Timings: 30, 60, 75, 90 and 120 seconds
7. Number of Dipping: 1
8. Various Annealing temperature: 600 °C and 800 °C
9. Various Time of Annealing : 1 minutes to 5 minutes (suitable to reach red hot nature)
10. Various Dipping Solution temperatures: 0 °C -100 °C and
11. Number of Annealing : 1

### 3. RESULTS & DISCUSSION

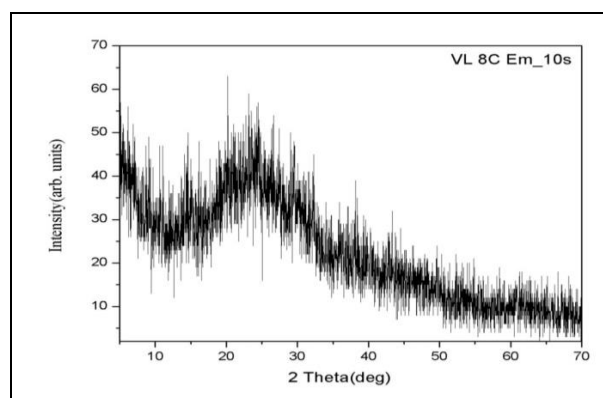
#### Characterization of SWCNTs

##### 3.1 Structural Characterization

X-Ray diffraction (XRD) is helpful in any process in which reactants undergo changes and give products of different chemical composition (or) Phases.

##### Gr (a) Grass

Fig. 1 revealed the X-ray diffract gram (XRD) of Gr (a) annealed at 800 °C (3 minutes) dipped in HNO<sub>3</sub> solution @ 45 °C (volume: 1 ml) for 90 seconds. The XRD explained the amorphous (non-crystalline) nature. Open air dry of fresh leaf after taken out from field and Annealing on Gr (a) grass leaf at 800 °C (3 min) leads to complete dryness of leaf. Due to that dehydration (removal of H<sub>2</sub>O molecules from C-H-O matrix) takes place in the leaf. Finally it allows carbon atoms only present in the leaf. After annealing, we have to immediately undergone that leaf by dipping into HNO<sub>3</sub> solution @ 45 °C (volume: 1 ml) for 90 seconds. Due to sudden cooling, the carbon lattices present in the leaf were cracked and split up into individual atoms. Finally that lattice formation is disappeared, leads to amorphous (non-crystalline) nature



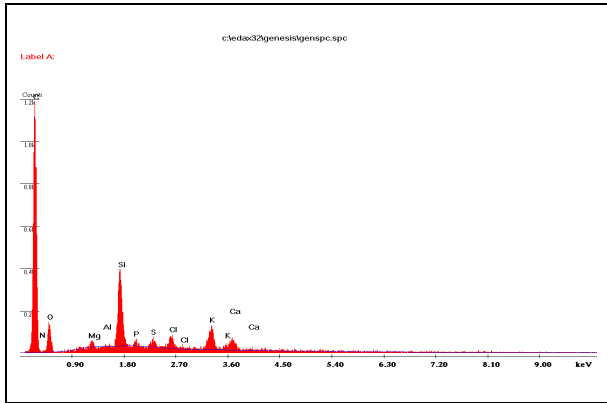
**Fig. 1: X-ray diffract gram (XRD) of Gr (a) annealed at 800 °C (3 minutes) dipped in HNO<sub>3</sub> solution @ 45 °C (Volume: 1 ml) for 90 seconds.**

##### 3.2. Compositional Characterization

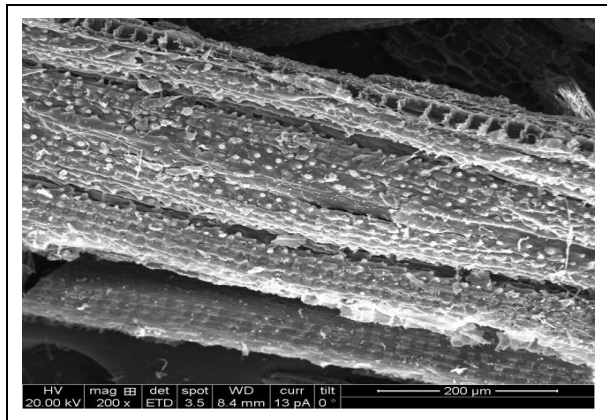
##### Gr (a) Grass

Fig.2 showed the EDAX Spectrum of a 600 °C (5 minutes) heated Gr (a) grass dipped in Mineral Water (Volume: 2.5 ml) for 120 seconds. It revealed the compositional elements present in the Gr (a) grass leaf. Presence of rich Carbon atoms (as indicated by 1<sup>st</sup> prominent peak in the EDAX spectrum) confirmed that the formed nano tubes are made up of carbon atoms. Which was authentically shows the formation of CNTs. Due to high temperature annealing, dehydration takes place, so H<sub>2</sub> atom was removed. Which was evidentially shown from the EDAX spectrum (i.e., H<sub>2</sub> peak was absent in the EDAX spectrum). Presence of O<sub>2</sub> atom in the EDAX spectrum evidentially shows that oxygen was injected / feed up during annealing. Presence of (Silicon) Si, (Oxygen) O shows that the grass leaf was enriched with SiO<sub>2</sub> (Soil) in which the grass was grown. Mg, Al, S, K, N, P, Cl and Ca proved that the Soil was enriched with them and roots of grass sucked these essential

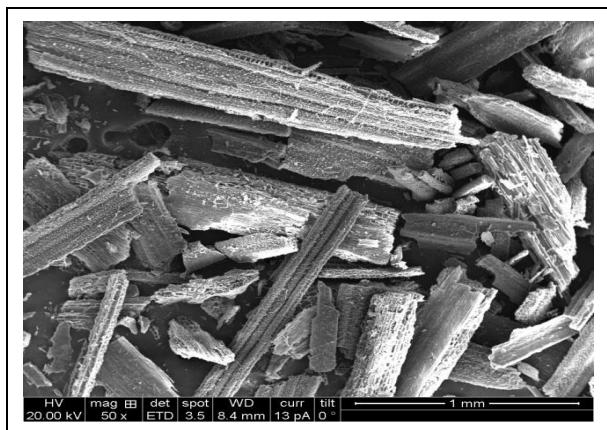
elements (nutrients) from soil for its growth and stability.



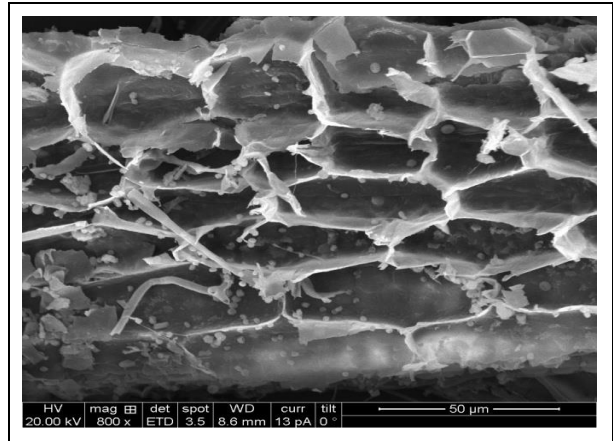
**Fig. 2:** EDAX Spectrum of a 600 °C (5 minutes) heated Gr (a) dipped in Mineral Water (Volume: 2.5 ml) for 120 seconds.



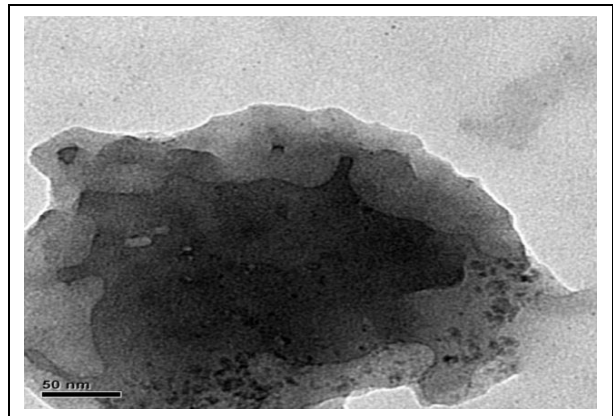
**Fig. 3:** SEM photograph of a 800 °C (4 minutes) annealed red hot Gr (a) dipped in Mineral Water (MW) Solution (volume: 2.0 ml) for 45 seconds, demonstrated pre-final, high grade shuffled/unordered horizontal/longitudinal Single walled Carbon Nano Tubes (SWCNTs) fabricated by rolled graphene sheets.



**Fig. 4:** SEM photograph of a 800 °C (3 minutes) annealed red hot Gr (a) dipped in Mineral Water (MW) Solution (volume: 1.5 ml) for 60 seconds, pictured out the eagle view of intermediate stage portion of high grade SWCNTs formed as well as an evidential proof for rolled graphene sheets.



**Fig. 5:** SEM photograph of a 800 °C (5 minutes) annealed red hot Gr (a) dipped in Mineral Water (MW) Solution (volume: 2.5 ml) for 30 seconds, flourished graphene sheets of super matured, high grade SWCNTs fabricated from hexagonal carbon matrices (an in-sight of an elongated damaged network).



**Fig. 6:** HRTEM image interpreted intermediate growth stage view of low grade homogeneous distribution of scattered pentagonal, hexagonal carbon matrices during sudden cooling- explode within poorly coagulated area, which acts as basic bricks i.e., building blocks of future Graphene sheets from 600°C (3 minutes) red-hot Gr (a) when dipping in NaOH (volume: 1.5 ml) for 60 Sec. kept at room temperature based on single time annealing and dipping process.

### 3.3 Surface Morphological Characterization

SEM studies were carried out with a JEOL JSM-840 operated at 20 KV.

#### Gr (a) Grass

Fig.3 expressed SEM photograph of a 800°C (4 minutes) annealed red hot Gr (a) dipped in Mineral Water (MW) Solution (volume: 2.0 ml) for 45 seconds. It demonstrated pre-final, high grade shuffled/unordered horizontal/longitudinal Single walled Carbon Nano Tubes (SWCNTs) fabricated by rolled graphene sheets. Fig.4 revealed SEM photograph of a 800 °C (3minutes)

annealed red hot Gr (a) dipped in Mineral Water (MW) Solution (volume: 1.5 ml) for 60 seconds. It pictured out the eagle view of intermediate stage portion of high grade SWCNTs formed as well as an evidential proof for rolled graphene sheets. Fig.5 enumerated SEM photograph of a 800 °C (5 minutes) annealed red hot Gr (a) dipped in Mineral Water (MW) Solution (volume: 2.5 ml) for 30 seconds. It flourished graphene sheets of super matured, high grade SWCNTs fabricated from hexagonal carbon matrices (an in-sight of an elongated damaged network).

### 3.4 Nanostructural Characterization

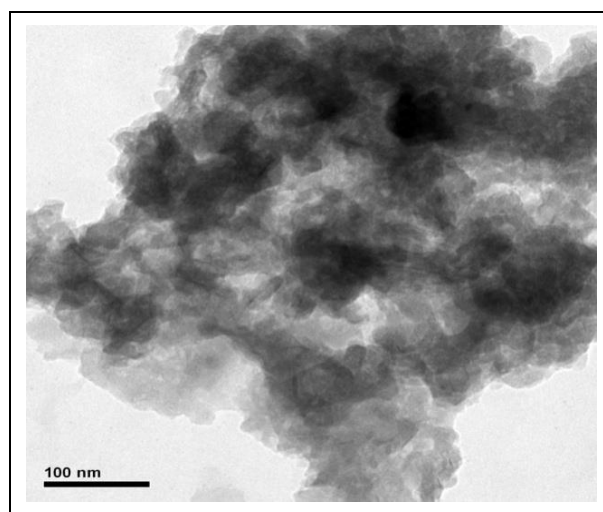
HRTEM studies were carried out with a JEOL-2010F, operated at 120 kV

#### Gr (a) Grass

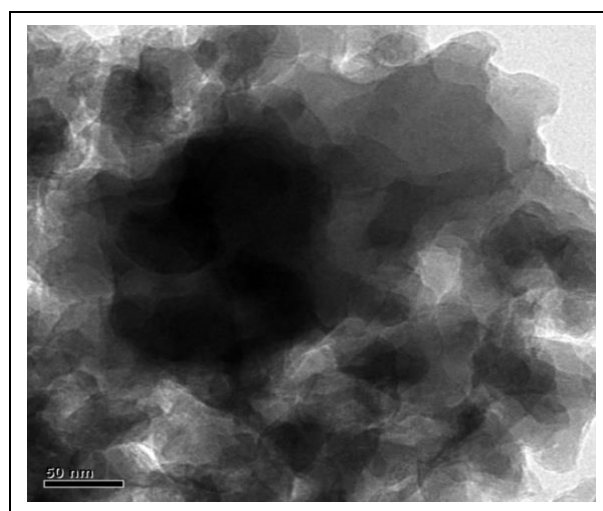
In fig. 6 HRTEM image interpreted intermediate growth stage view of low grade homogeneous distribution of scattered pentagonal, hexagonal carbon matrices during sudden cooling-explode within poorly coagulated area, which acts as basic bricks i.e., building blocks of future Graphene sheets from 600 °C (3 minutes) red-hot Gr (a) grass when dipping in NaOH (volume: 1.5 ml) for 60 Sec., kept at room temperature based on single time annealing and dipping process. In fig.7 HRTEM image illustrated the pre-final growth stage view of moderate grade in-homogeneous distribution of scattered pentagonal and hexagonal carbon matrices during sudden cooling-explode, which acts as basic building blocks of future graphene sheets from 600 °C (4 minutes) red-hot Gr (a) when dipping in HW+D2W (volume: 2.0 ml) for 90 Sec., kept at room temperature based on single time annealing and dipping process.

In fig.8 HRTEM image expressed final growth stage view of low grade in-homogeneous distribution of scattered pentagonal and hexagonal carbon matrices during sudden cooling-explode, which acts as basic building blocks of future graphene sheets from 800 °C (1 minute) red-hot Gr (a) grass when dipping in NaOH (volume: 0.5 ml) for 120 Sec. kept at room temperature based on single time annealing and dipping process. In fig.9 HRTEM image confirmed the intermediate tubular origination (in-situ formation and rolling of graphene sheets) from moderate grade in-homogeneously distributed, scattered pentagonal and hexagonal carbon matrices during sudden cooling-explode, (which acts as basic building blocks of graphene sheets) of 800 °C (3 minutes) red-hot Gr (a) grass when dipping in mineral water (HW+D2W) (volume: 1.5 ml) for 75 Sec. kept at room temperature based on single time annealing and dipping process. In fig.10 HRTEM image confirmed the super final matured tubular formation from high grade pentagonal and hexagonal carbon matrices during sudden cooling-explode, (which acts as basic building blocks of graphene sheets) of 800 °C (5 minutes) red-hot Gr (a)

grass when dipping in mineral water (MW) (volume: 2.5 ml) for 30 Sec. kept at room temperature based on single time annealing and dipping process.



**Fig. 7:** HRTEM image illustrated the pre-final growth stage view of moderate grade in-homogeneous distribution of scattered pentagonal and hexagonal carbon matrices during sudden cooling-explode, which acts as basic building blocks of future graphene sheets from 600 °C (4 minutes) red-hot Gr (a) when dipping in HW+D2W (volume: 2.0 ml) for 90 Sec. kept at room temperature based on single time annealing and dipping process.



**Fig. 8:** HRTEM image expressed final growth stage view of low grade in-homogeneous distribution of scattered pentagonal and hexagonal carbon matrices during sudden cooling-explode, which acts as basic building blocks of future graphene sheets from 800 °C (1 minute) red-hot Gr (a) when dipping in NaOH (volume: 0.5 ml) for 120 Sec. kept at room temperature based on single time annealing and dipping process.

Parameters, as inferences from above characterizations were calculated, tabulated and graphically emphasized. The effects of optimizations parameters like pH of the various dipping solutions

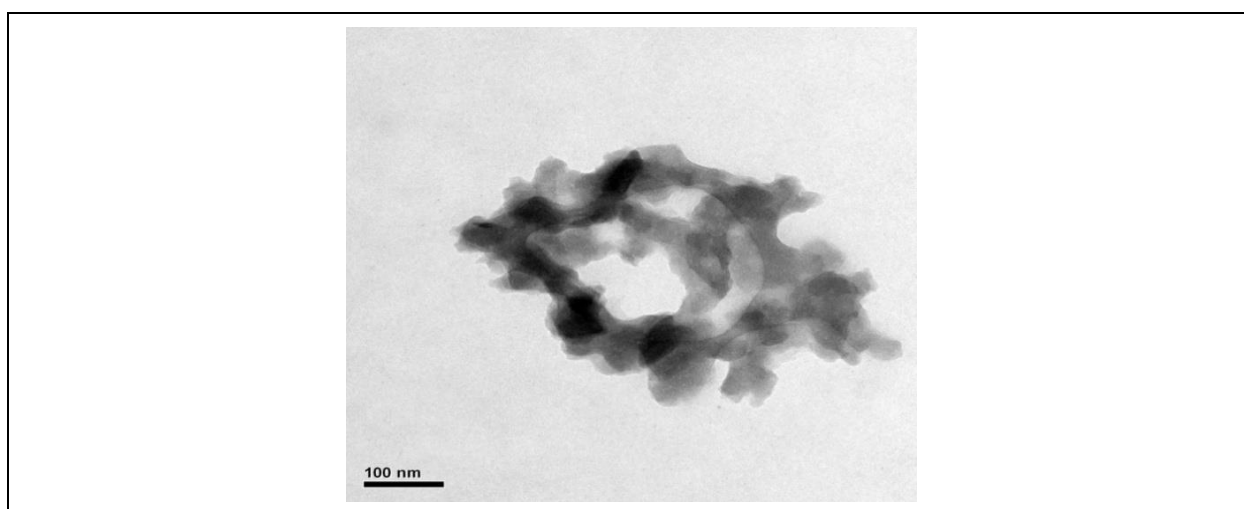
(acidic, basic and neutral), volume of dipping solutions, various types and parts of the materials, various dipping timings, number of annealing and dipping, various annealing temperature, various time of annealing and various dipping solution temperatures on structural, compositional, surface morphological, nano-structural characterizations of materials and on high grade SWCNTs growth with high yield were studied intensively. Correlation studies between these characterization inferences (such as grain size, purity) and optimization parameters were carried out with a high light on yield of high grade SWCNTs. Beyond all of these, we have carried out a new feasibility study at first time, which comprises the possible usage of precursor organic carbon sources for high grade SWCNTs with high yield via a low cost technique and methodology as value in commercial efforts.

#### 4. CONCLUSION

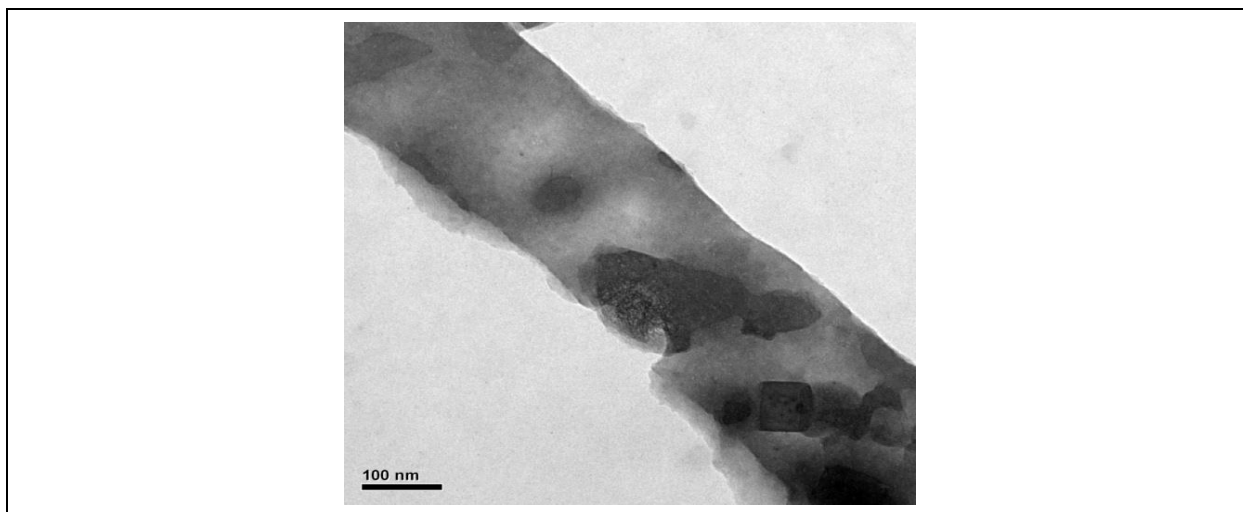
As a result of this over all study, Gr (a) grass plays as a most optimum material for high grade SWCNTs growth. Generally, we may understand that specialized materials play as most optimum materials than fibrous and conventional materials. But among

fibrous materials, Gr(a) grass plays a dominant role than Gr(k) grass. Also any Dipping Solution (of Volume: 2.5 ml) having pH=7, i.e., neutral solution (normally maintained at room.temp. RT) (with 30 Seconds as optimum time of dipping) act as an optimum medium which provides suitable environment for high grade, large quantity SWCNTs growth. Similarly 800<sup>o</sup>C (having annealing time: 3 minutes) provides suitable background thermal history for high grade, large quantity SWCNTs growth based on single time annealing and dipping process. High purity precursor material yield high grade SWCNTs.

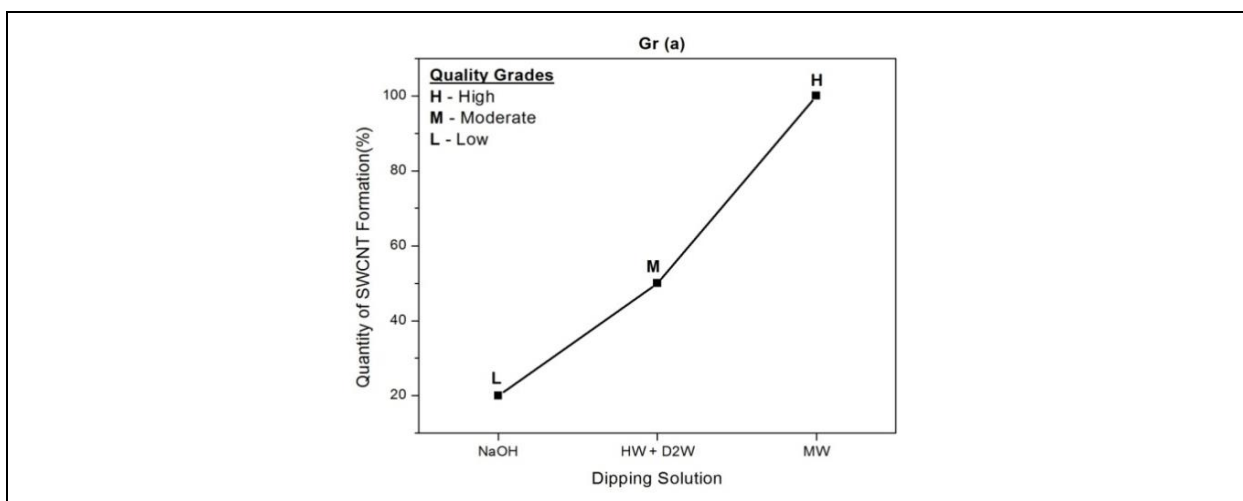
Fig. 11 picture out the Plot between quantity of SWCNTs formation (%) and Dipping solution with an insight into quality grades of SWCNTs grown from Gr (a) grass. The Fig. depicts that neutral dipping solution provides a suitable environment for high grade SWCNTs growth in Gr (a) grass varieties. All of these works have value in nanotechnology, nano-materials processing and device fabrication efforts either as a technical or scientific basis, also as a contribution to the present day state of the art of nano drug delivery system.



**Fig. 9: HRTEM image confirmed the intermediate tubular origination (in-situ formation and rolling of graphene sheets) from moderate grade in-homogeneously distributed, scattered pentagonal and hexagonal carbon matrices during sudden cooling-explode, (which acts as basic building blocks of graphene sheets) of 800<sup>o</sup>C (3 minutes) red-hot Gr (a) when dipping in mineral water (HW+D2W) (volume: 1.5 ml) for 75 Sec. kept at room temperature based on single time annealing and dipping process.**



**Fig. 10:** HRTEM image confirmed the super final matured tubular formation from high grade pentagonal and hexagonal carbon matrices during sudden cooling-explode, (which acts as basic building blocks of graphene sheets) of 800°C (5 minutes) red-hot Gr (a) when dipping in mineral water (MW) (volume: 2.5 ml) for 30 Sec. kept at room temperature based on single time annealing and dipping process.



**Fig. 11:** Plot between quantity of SWCNTs formation (%) and Dipping solution with an insight into quality grades of SWCNTs grown from Gr (a).

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### CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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