A NEW FABRICATION OF HIGH GRADE SWCNTS FROM PLANTAIN TREE LEAVES FOR RNA DELIVERY SYSTEM -A NOVEL FEASIBILITY STUDY

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ABSTRACT

Synthesis of high grade SWCNTs from natural organics i.e., Plantain tree leaves by a novel modified AC method – VSA methodology (with KRS or NTFDS theory) was newly adopted in this present work for possible application towards RNA 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 novel feasibility study at first time, which comprises the possible usage of precursor organic carbon sources i.e., Plantain tree leaves for high grade SWCNTs with high yield via a low cost technique and methodology as value in commercial efforts.

Keywords: *Modified AC method, VSA methodology, NTFDS theory, Natural organics, Plantain tree leaves, XRD, EDAX, SEM, HRTEM, SWCNTs, RNA delivery system*

1. INTRODUCTION

The present work showed that SWCNTs obtained by open air annealing and cooling of leaves of Plantain tree leaves. The present work made a new break through via plays an alternative method to conventional, traditional methods such as arc discharge, laser ablation, metal catalysts, pyrolysis, varieties of CVD methods and also removes the usage of synthetic chemicals. The modified AC method [Zhenhui Kang et al, 33] – VSA methodology (with KRS or NTFDS theory) was adopted in this present work for the preparation of CNTs from natural organics. The entire steps such as Precursor materials selection with cleaning, Annealing, Sudden cooling, Interaction between red hot natural organic carbon resource materials and Dipping solutions (DS) [including Nano Thermo Fluid Dynamics (NTFDS) and Nano-drilling process] involved in this process were explained. The characterizations performed on outcome products were internationally accepted, standard methods as followed by field specialists through out the world [1-33].

2. EXPERIMENTAL DETAILS

Precursor carbon source materials i.e., Plantain tree leaves collected from nature, cleaned in water and dried in open air. These materials were used without further purification. Then the materials were open air annealed (upto red hot) in a muffle furnace at various temperatures viz., 600^0C and 800^0C 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_2O_2), Nitric Acid (HNO_3), Sulphuric Acid (H_2SO_4), 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 0^0C to 100^0C, 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 and 2.5 ml,3. Various types of materials: conventional: varities of plants, trees: Plantain tree, 4. Various Parts of the materials: leaves, 5. Various Dipping solutions: Sodium hydroxide (NaOH), Hydrogen peroxide (H_2O_2), Nitric Acid (HNO_3), Sulphuric Acid (H_2SO_4), 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 seconds, 45 seconds, 60 seconds, 75 seconds, 90 seconds and 120 seconds., 7. Number of Dippings: 1, 8. Various Annealing Temperatures: 600^0C and 800^0C, 9. Various Time of Annealing: 1 minute to 5 minute, 10. Various Dipping Solution temperatures: 0^0C to 100^0C., 11. Number of Annealing: 1

3. RESULTS AND DISCUSSION

Characterization of CNTs

3.1 Structural Characterization

Plantain tree leaf

Fig. [3.1.1] picture out the X-ray diffract gram (XRD) of Plantain leaf annealed at 800^{o}C (3 minutes) dipped in NaOH solution maintained at 45^{o}C (volume: 0.5 ml) for 60 seconds shows amorphous (non-crystalline) nature. Open air dry of fresh leaf after taken out from field and annealing on Plantain leaf at 800^{0}C (3 min) leads to complete dryness of leaf. Due to that dehydration (removal of H_2O 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 NaOH solution (60 seconds). Due to sudden cooling, the carbon lattices present in the leaf were cracked, split up into individual atoms. Finally that lattice formation is disappeared, leads to amorphous (non-crystalline) nature

3.2 Compositional Characterization

Plantain tree leaf

Fig. [3.2.1] explored EDAX Spectrum of a800^{0}C (1 minute) heated plantain tree leaf dipped in NaOH Solution (volume: 1.5 ml) (120 Seconds). EDAX Studies on 800^{0}C (1 minute) heated Plantain tree leaf dipped in NaOH Solution (2 minutes) shows compositional elements present in the Plantain leaf (Fig.6). Presence of rich Carbon atoms (1st prominent peak in EDAX spectrum) confirmed that the formed tubes are made up of carbon atoms. Which was authentically shows the formation of CNTs. Due to high temperature annealing, dehydration takes place, H_2 atom was removed. Which was evidentially shown from the EDAX spectrum (i.e., H_2 not found in the EDAX spectrum). Presence of O_2 atom in the EDAX spectrum evidentially shows that oxygen was injected / feed up during annealing. Presence of (Silicon) Si, (Oxygen) O shows that the leaf was enriched with SiO_2 (Soil) in which the tree was grown. Mg, Al, S, K, N, Na, P, Cl and Ca proved that the Soil was enriched with fertilizer and roots of tree sucked these essential elements (nutrients) from soil for its growth and stability.

3.3 Surface Morphological Characterization

Plantain tree leaf

SEM images of 800^{o}C (3 minutes) heated Plantain leaves dipped in NaOH solution (30 and 60 seconds) revealed the formation of rolling of graphene sheets to make SWCNTs and hexagonal carbon network (Refer.Fig.3.3.1 – 3.3.2) (longitudinal view and top view). The images Showed NaOH solution acts as a optimum medium (any solution which has pH >7) for intermediate stage formation (i.e., rolling) of graphene sheets to form longitudinal SWCNTs in Plantain leaf. The images depict the matured hexagonal carbon (lattice network) matrix present in the graphene sheets to form SWCNTs by rolling, which shows that NaOH solution is an optimum medium for SWCNT growth. From the SEM studies, we know that, the single time dipping and minimum time of dipping in particular solution leads to the formation of SWCNTs. 800^0C act as a suitable growth environment for SWCNTs.

Fig. [3.3.1]. emphasized SEM photograph of a 800^oC (3 minutes) heated red hot Plantain tree leaf dipped in Sodium Hydroxide (NaOH)Solution (volume: 1.5 ml) for 60 seconds. It shows rolling of graphene sheets to form super matured high grade SWCNTs (longitudinal view). Fig. [3.3.2] explained SEM photograph of a 800^oC (3 minutes) heated red hot Plantain tree leaf dipped in Sodium Hydroxide (NaOH)Solution (volume: 2.5 ml) for 30 seconds. It shows super matured graphene sheet as a network of hexagonal carbon matrices to form super matured SWCNTs (longitudinal view).

3.4 Nanostructural Characterization

Plantain tree leaves

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

In Fig. [3.4.1], HRTEM image shows an intermediate growth stage portion of a low grade, very poorly coagulated hexagonal carbon matrices during 600^0C (3 minutes) red-hot Plantain leaves when dipped in ice water mixed double distilled water(IceW+D2W) (volume: 2 ml) solution for 60 seconds based on single time annealing and dipping process. In Fig. [3.4.2], HRTEM image shows an intermediate growth stage portion of a moderately grown, poorly coagulated hexagonal carbon matrices during 600^0C (3 minutes) red-hot Plantain leaves when dipped in double distilled water (D2W) (volume: 1.5 ml) solution for 60 seconds based on single time annealing and dipping process. In Fig. [3.4.3], HRTEM image shows an semi-matured growth stage portion of a low grade, poorly coagulated hexagonal carbon matrices during 800^0C (2 minutes) red-hot Plantain leaves when dipped in ice water mixed double distilled water (IceW+D2W) (volume: 1.5 ml) solution for 75 seconds based on single time annealing and dipping process.

In Fig. [3.4.4], HRTEM image shows semi-matured, moderate coagulation of hexagonal carbon building blocks (due to sudden cooling inside dipping solution) from 800^0C (4 minutes) red-hot plantain leaves when dipped into double distilled (D2W) water (volume: 2 ml) for 45seconds,based on single time annealing and dipping process. In Fig. [3.4.5], HRTEM image shows shuffled vertical and bended wave like horizontal super matured SWCNTs (having inner diameter approximately 0.16 nm i.e., 1.6 Å) derived from homogeneously distributed matured hexagonal carbon matrices (via graphene layer formation and rolling) during 800^0C (3 minutes) red-hot Plantain leaves when dipped in sodium hydroxide (NaOH) (volume: 2.5 ml) solution for 30 seconds based on single time annealing and dipping process. 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. Parameters, as inferences from above characterizations were calculated, tabulated and graphically emphasized. 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 novel feasibility study at first time, which comprises the possible usage of precursor organic carbon sources i.e., margosa (neem tree) leaves for high quality SWCNTs with high yield via a low cost technique and methodology as value in commercial efforts.

4. CONCLUSION

In this over all study, Plantain leaves plays as a most optimum material for high grade SWCNTs growth among conventional materials. 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 800^0C (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. High purity precursor material yield high grade SWCNTs.

Plantain tree leaves

Fig. [4.1] interpreted the effects of dipping solution on Quantity of SWCNTs formation (%) with an eagle view on Quality grades of SWCNTs grown from Plantine leaves. The graph showed NaOH solution acts as a optimum medium (any solution which has pH >7) for getting high grade SWCNTs in Plantain leaf than neutral dipping solution having pH =7. 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 RNA delivery system

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REFERENCES

1. S. Iijima , Nature 354, 56 (1991) 391
2. Iijima, S.; Ichihashi, T. Nature 363 (1993) 603
3. P.M.Ajayan and T.W.Ebbesen, Nanometre size tubes of carbon, Rep.Prog.Phys., 60 (1997) 1034-1040
4. P.M.Ajayan and S.Iijima, Nature 361,333 (1993) 392
5. B.I.Yakobson, R.E.Smalley, American Scientist 85, 324 (1997) 391
6. M.S.Dresselhaus, Science of Fullerenes and Carbon nanotubes, Academic Press, New York, (1996) 391.
7. T.W.Ebbesen, Carbon nanotubes: Preparation and properties, CRC Press, Boca Raton, (1997) 391
8. C.Dekker, Phys. Today, 22 (1999) 391
9. E.Dujardin, T.W.Ebbesen, T.Hiura, K.Tanigaki, Science 265 (1994) 392
10. P.Collins, A.Zettl, Appl.Phy.Lett, 69 (1996) 396
11. K.A.Dean, B.R.Chalamala, J.Appl.Phys 85,3832 (1999) 396
12. M.Winter, J.Besenhard, K.Spahr, P.Novak, Adv.Mater.10,725 (1998) 402
13. M.S.Dresselhaus, K.A.Williams, P.C.Eklund, MRS Bull, 24,11,45 (1999) 404
14. P.Calvert, Nature 399,210 (1999) 409
15. Shaoping Xiao and Wenyi Hou, Studies of Size effects on CNTs : mechanical properties by using differential potential functions, Fullerenes,nanotubesn carbon nanostructures,14 (2006) 9-16.
16. Zhiyang Rong, Fabrication and characterization of CNTs for Bio-medical Applications,

M.Sc Thesis,Aug.,2008.

17. Rostam Moradian and Ali Fathalian, Ferromagnetic semiconductor single wall CNTs, Nanotechnology 17 (2006) 1835-1842

18. Chun Li et al., Field emission from carbon nanotube bundle arrays grown on self - aligned ZnO nanorods, nanotechnology 18 (2007), 155702

19. M.P.Rossi et al., Environmental SEM Study of water in carbon nanopipes, Nano Lett.,4 (2004) 989-993

20. Majumder M,et al.,Nanoscale hydrodynamics: enhanced flow in carbon nanotubes, nature 383 (2005) 438-444

21. D.Mattia, G.Korneva and Y.Gogotsi, Multifunctional CNT with nanoparticles embedded in their walls, Nanotechnology 18 (2007) 155305

22. Guoyong Xu et al., Functionalised CNTs with polystyrene-block-poly by in-situ RAFT Poymerization, Nanotechnology, 18 (2007) 145606

23. Teh-Hwa Wong et al., Nanosecond Laser pulse - induced electron emission from MWCNTs films, Nanotechnology, 18 (2007) 135705.

24. H.Kuromochi et al., Why nano-oxidation with CNT probes is so stable : I.Linkage between hydrophobicity and stability, Nanotechnology, 18 (2007) 135703.

25. J.Bond et al., CVD of SWCNTs freely suspended over NT supports, Nanotechnology, 18 (2007) 135603

26. Q.Z.Xue, Model for the effective thermal conductivity of CNT Composites, Nanotechnology, 17 (2006) 1655-1660.

27. Wang. S et al., Statistical characterization of SWCNTs length distribution, Nanotechnology, 17 (2006) 634-639.

28. Chiu.P.W et al., Interconnection of CNTs by chemical functionalization,Appl.Phy.Lett 18 (2002) 3811

29. Y.Wang et al, Functionalization of CNTs with amines and enzymes, Chem.Phys.Lett 402 (2005) 96

30. Shiren Wang et al, Effective amino - functionalization of CNTs for Reinforcing epoxy polymer composites, Nanotechnology, 17 (2006) 1551-1557.

31. K.Safarova et al, Usage of AFM, SEM, TEM for the research of CNTs, Mod.Res.and Edu.Topics in Microscopy, (2007) 513

32. S. Bellucci et al, AFM Characterizations of CNTs, Journal.Phy.Conf.Series 61(2007) 99-104

33. Zhenhui Kang et al, Obtaining CNTs from grass,Nanotechnology,16 (2005) 1192-1195.