

List of research publications

Paper published

- [1] **A. Nath**, A. Das, S. Deb, C.R. Bhattacharjee, J. Rout
‘Green synthesis of novel antioxidant luminescent silica nanoparticle embedded carbon nanocomposites from a blue-green alga’
Green Process. Synth., **2016**(doi: 10.1515/gps-2015-0124).
- [2] **A. Nath** , D. D. Purkayastha , M. Sharon, C.R. Bhattacharjee
‘Catalyst free low temperature synthesis and antioxidant activity of multiwalled carbon nanotubes accessed from *ghee*, clarified butter of cow's milk’
Mater. Lett., **2015**, **152**, 36-49.
- [3] C. R. Bhattacharjee, S. B. Paul, **A. Nath** , S. Choudhury, P. N. Choudhury
‘Synthesis, X-ray diffraction study and antimicrobial activity of calcium sulphate nanocomposite from plant charcoal’
Materials, **2009**, **2**, 345- 352.
- [4] C. R. Bhattacharjee, **A. Nath**, B.T.Mukherjee, D. D. Purkayastha, M. Sharon, M. Sharon
‘Synthesis and characterization of carbon nanotubes using a natural precursor: turpentine oil’
Sci. J. UBU., **2011**, **2**(1), 36-42

Papers communicated

- [1] **A. Nath**, N. Sinha, S. Hazra, M. Sharon, N. N. Ghosh, C. R. Bhattacharjee
‘Photocatalytic activity of carbon nanoflakes accessed from *Crassocephalum crepidioides* seed hairs’
New Carbon Mater., **2015**
- [2] **A. Nath** , N., Misra , M. Sharon, C.R. Bhattacharjee
‘Biogenic synthesis and electrochemical behaviour of carbon nanospheres from seeds of a tropical ornamental plant’
Carbon Lett., **2016**

- [3] **A. Nath**, D., Mohanta, M. Sharon, C.R. Bhattacharjee
'Synthesis and electrochemical behaviour of calcium carbonate nanoflakes accessed from bond paper waste'
Mater. Lett.,2016
- [4] J. Rout, **A. Nath**, A. Das, B. Sarma, S. Deb, C.R. Bhattacharjee,
'Biogenic synthesis of antioxidant carbon-silica nanocomposite from a green alga, *Trentepohlia aurea*'
Carbon Lett.,2016
- [5] **A. Nath**, A. Das, S. Deb, C.R. Bhattacharjee, J. Rout,
'Biogenic synthesis of carbon-silica nanocomposite from a green alga, *spirogyra* sp.'
New Carbon Mater.,2016

Book Chapters

- [1] C.R. Bhattacharjee, **A. Nath** (2011)
Chapter'Synthesis and characterisation of inorganic nanocomposites from plant- based sources'in - Status and conservation of Biodiversity in North East India.Swastik Publications, New Delhi, India, pp 88-96. **(ISBN: 978-93-81084-10-6)**.
- [2] C.R. Bhattacharjee, **A. Nath**, P .Paul, N. Sinha, N. Bhowmik (2013)
Chapter'Synthesis and characterization of carbon nanomaterials from natural fibres: *Bougainvillea spectabilis* (paper flower) and *Cocos nucifera* (coconut)'in Emerging Areas of Research & Development in Chemical and Physical Sciences in North East India. Sungraphics, Silchar, Assam, India, pp 126-137. **(ISBN: 978-81- 908204-3-3)**.

List of workshops/ seminars/ conferences/ training

1. Presented a paper entitled 'Synthesis, antioxidant and electrochemical study of unusual carbon nanostructures from plant seeds and fibres' in **National seminar** on computational research and its development in experimental sciences, CRIDES-2016 at Karimganj College, Karimganj, Assam during 12-14 March, 2016.
2. Presented a paper entitled 'Catalyst free low temperature synthesis and antioxidant activity of multiwalled carbon nanotubes accessed natural precursors' in 4th **International Conference** on 'Advanced Nanomaterials and Nanotechnology, ICANN-2015' at IIT Guwahati, India during 8-12 Dec, 2015.
3. Presented a paper entitled 'Synthesis and anti oxidant behaviour of Carbon Nano Materials synthesised from plant based sources' in UGC sponsored **National Seminar** on Biodiversity Vis-à-vis Development at S.S. College, Hailakandi, Assam on 14-15 Oct, 2015.
4. Presented a paper entitled 'Synthesis and characterization of carbon nanomaterials (CNMs) from plant fibres, seeds and oils' in **Regional Seminar** on Modern Research in Chemical Sciences at Karimganj College, Karimganj, Assam on 17 Jan, 2015.
5. Presented a paper entitled 'Nanotechnology in Diagnosis and Treatment of Cancer' at **International Virtual Congress** organised by International Science Congress Association on 5-10 June, 2014.
6. Presented a paper entitled 'Synthesis and applications of carbon nanomaterials from renewable feed stock' in **International Conference** on Material Chemistry at Department of Chemistry, **ShahJalal University of Science and Technology, Sylhet, Bangladesh** on 6-8 Dec, 2014.
7. Presented a paper entitled 'Smart Chemistry with reference to Nano world' in TSTEC sponsored **Popular Science Talk-2014** organized by and Government Degree College, Dharmanagar, North Tripura on 7 Nov, 2014.
8. Presented a paper entitled 'Chemitoons: A presentation which breaks the rule' in UGC sponsored **National Seminar** at Cachar College, Silchar, Assam on 25-26 Mar, 2013.
9. Presented a paper entitled 'Synthesis, capacitance and antioxidant behaviour of Carbon Nano Fibres from Plant Fibres by Chemical vapour deposition technique' in **International Conference** on Material Science (ICMS-2013) at Department of Physics, Tripura University, Tripura on 21-23 Feb, 2013.

10. Presented a paper entitled 'Plant Biodiversity of North Eastern Region of India- A Boon for Nanotechnology' in UGC sponsored **National Seminar** on Biodiversity Conservation and its Future Scenario at S. S. College Hailakandi, Assam on 20-21Feb, 2012.
11. Presented a paper entitled 'Synthesis and characterization of carbon nanomaterials from plant fibres and seeds' in **International Conference** at Department of Life Sciences and Bioinformatics, Assam University, Silchar on 16-17 March, 2012.
12. Presented a paper entitled 'Synthesis and antimicrobial studies of silver Nanoparticles from Tamarind juice, jujube juice' in UGC sponsored **National Seminar** on 'Biodiversity Conservation and its Future Scenario' at S. S. College, Hailakandi, Assam on 20 -21 Feb, 2012.
13. Presented a paper entitled 'Synthesis, Capacitance and Antioxidant Behaviour of Carbon Nanofibres from Inflorescence of Pampas Grass (*Cortaderiaselloana*) via Chemical Vapour Deposition Technique' in the **International Conference** on 'Supramolecules and Nanomaterials- Research and Applications' at Gujarat University, Ahmedabad, India on 6-8 Feb, 2012.
14. Presented a paper entitled 'Plant Biodiversity of North Eastern Region of India and Bangladesh – A Boon for Nanotechnology' in **International Conference** on Exploring Sub-Regional cooperation in the Context of India-Bangladesh Relations: Society, History, Science and Culture' at Assam University, Silchar, India during 22-24th Jan, 2012..
15. Presented a paper entitled 'Synthesis and characterization of carbon nanomaterials from natural fibres: paper flower and coconut fibres' in UGC sponsored **National Seminar** on 'Emerging Areas of research and developments in chemical and physical sciences in north-east India' at S. S. College, Hailakandi, Assam during 16th -18thoct, 2012.
16. Presented a paper entitled 'Synthesis and Characterization of Nanoparticles from L-Methionine-Fluoro Complexes of Copper(II)' in UGC, BRNS, DST and INSA sponsored **National Seminar** on 'Frontiers of Research in Physics' at Karimganj College, Karimganj, Assam during 22-24 Dec, 2011.

17. Presented a paper entitled 'Synthesis of carbon nanomaterials from fibres and seeds and study of their hydrogen gas adsorption' in the 2nd **International Conference** on 'Advanced Nanomaterials and Nanotechnology, ICANN-2011' at IIT Guwahati, India during 8-10th Dec, 2011.
18. Presented a paper entitled 'Nanocubes and Nanospheres from Plant Seeds' and received 2nd best poster presentation award in the One day **National Workshop** on 'Soft matter' at Assam University, Silchar, on 17th Sept., 2011.
19. Presented a paper entitled 'Synthesis and Characterization Carbon Nanotubes from Natural Precursor, Turpentine Oil' in the UGC, CSIR and DST sponsored **National Seminar** on 'Environmental Chemistry and Human Health' at Karimganj College, Karimganj, Assam during 12-14 Feb, 2011
20. Presented a paper entitled 'Synthesis and Characterization of Carbon Nanofibres from Pampas Grass and Red Algae' in the UGC sponsored **National Seminar** on 'Contemporary Trends of Research in Physical Sciences' at G. C. College, Silchar on 11-12 Feb, 2011.
21. Presented a paper entitled 'Nano Technology and the Development of North East India' in the UGC sponsored **National Seminar** on 'Problems and Prospects of Development in the North Eastern Region' at S. S. College, Hailakandi on 1st and 2nd Feb, 2010.
22. Presented a paper entitled 'Synthesis and Antimicrobial Activities of Carbon Nanomaterials derived from Plant based Sources' paper in the **International Conference** on 'Recent Trends in Medicinal and Aromatic Plant Researches, RTMAPR-2010' at Assam University, Silchar during 1-5th Dec, 2010.
23. Presented a paper entitled 'Synthesis and Characterization of Carbon Nanomaterials from Natural fibers and oils' in IUPAC Sponsored **International Conference** on 'Nanomaterials and Nanotechnology, NANO-2010' at KSRCT, Tiruchengode, Tamilnadu, India during 13-16th Dec, 2010.
24. Presented a paper entitled 'Prospects of Traditional Knowledge on Health Care of the Tribes of North- East India' in the UGC sponsored **National Seminar** on 'Health and Sanitation- an Insight into North East Region of India' at B. B. M. College, Agartala, on 7th and 8th March, 2009.

25. Presented a paper entitled 'Synthesis and Characterisation of Inorganic Nano Composites from Plant based Sources' in the **National Conference** on 'Recent Trends in Biodiversity Researches, RTBR-2009' at AU, Silchar, during 16-18 March, 2009.
26. Presented a paper entitled 'Fabrication of Carbon Nanomaterials by Chemical Vapour deposition from Natural Fibers and Oils' in the UGC sponsored **Regional Seminar** on 'Recent Trends in Chemistry' at Govt. Degree College, Dharmanagar, North Tripura on 12th and 13th Sep, 2009.
27. Presented a paper entitled 'CVD- A Novel Synthetic Route for CNT' in **National Seminar** on 'Contemporary Areas in Physical Sciences and Life Sciences' by Karimganj College and SINP, Kolkata at Karimganj College, Karimganj, Assam on 26th and 27th Nov, 2009.
28. Presented a paper entitled 'Chemical Synthesis and Antimicrobial Activity of NiO and ZnO nanomaterials' in the **International Conference** on 'Advanced Nanomaterials and Nanotechnology, ICANN-2009' at IIT Guwahati, India during 9-11th Dec, 2009.
29. Presented a paper entitled 'Biodiversity and sustainable development - A critical analysis with special reference to North east India' in UGC sponsored **National Seminar** on 'Biodiversity Conservation and its Future Scenario' at S. S. College, Hailakandi, Assam on 20 -21 Feb, 2012.
30. Resource Lecture at DBT sponsored three day workshop on 'Recent trends on biotechnology research' at Biotech Hub, G.C. College, Silchar during 24-26 Dec, 2015.
31. Participated in a **International Conference** on 'Global Ecosystems, Biodiversity, and Environmental Sustainability in the 21st Century(ICGEBENS-2012)' at Dept. of Ecology and Environmental Science, Assam University, Silchar, India during 15-17th Feb, 2012.
32. Participated in a DBT sponsored Invited talk on Green Chemistry Organised by Department of Chemistry at S.S. College, Hailakandi on 14th March, 2015.
33. Participated in a Workshop on Recent Trends in 'Synthesis of Chemical Compounds and their application in Science and Technology' at N.I.T. Silchar on 5-7 May, 2014.

34. Participated in a UGC sponsored 7 days workshop on Recent Trends of Research and its applications in Physical Sciences organized by Department of chemistry and Physics, S.S. College Hailakandi on 21-27 Jan, 2014.
35. Participated in a DBT sponsored Hands on Training on Some Basic techniques in Molecular Biology organised by Institutional Bio Tech Hub, at S.S. College, Hailakandi, Assam during 22-23 March, 2013.
36. Participated in a **National workshop** on Modern Trends in Chemistry and Chemistry Education, organized by Department of chemistry, University of North Bengal, West Bengal on 22-23 Nov, 2012.
37. Participated in a UGC sponsored **National Seminar** on 'Socio-Economic and Cultural Problems and Its solution in Development of Tribals of North East Region of India' at S.S.College, Hailakandi, Assam during 16th -17th Feb, 2012.
38. Participated in a UGC sponsored **National Seminar** on 'Linguistic Movements and their Future in Southern Assam at S. S.College, Hailakandi, Assam on 19th and 20th Aug, 2011.
39. Participated in a UGC sponsored **National Seminar** on 'Current Trends in Condensed Matter Physics (CTCMP-2011)' at Assam University, Silchar during 3-5th Feb, 2011.
40. Participated in a UGC sponsored National Seminar on 'Human Rights' at R. K Nagar College, R. K. Nagar, Karimganj, Assam on 14th and 15th Sep, 2010.
41. Participated in a Research Cell sponsored Inter Departmental Seminar on Science and Humanity at S.S.College, Hailakandi, Assam on 30th Sep, 2010.
42. Participated in a UGC sponsored **National Conference** on 'Recent Advances in Mathematical Sciences and Their Application (RAMSA-10)' at AssamUniversity, Silchar during 25-27th Nov, 2010.
43. Participated in a **Regional Seminar** on 'Intellectual Property and Innovation Management Era' by AssamUniversity, Silchar and National Research Development Corporation (NRDC) at AssamUniversity, Silchar on 12th and 13th Jan, 2009.
44. Participated in a UGC sponsored **National Seminar** on 'Economic Development and Environmental Pollution in India' at Lala Rural College, Hailakandi, Assam on 9th and 10th Nov, 2009.

45. Presented a paper entitled 'Relevance of Rabindranath Tagore in Modern Science-A critical Analysis' in UGC sponsored **National Seminar** on 'Relevance of Tagore in Present Days' at S. S. College, Hailakandi on 18-19 Feb, 2012.
46. Participated in a 'Frontier Lecture Programme on Astro- Particle Physics and Structural Genomics and Proteomics' by S. S. College and SINP, Kolkata at S.S.College, Hailakandi on 21st Aug, 2009.
47. Participated in a 15 Days Research Training on **Synthesis of Carbon nanomaterials from plant based precursors by CVD technique and Hydrogen adsorption using Sievert's apparatus and capacitance measurement using potentiostat** at NSNRC for Nanotechnology and Bionanotechnology, Ambernath, Maharashtra from 6th Oct to 20th Oct, 2011.
48. Participated in a One month Research Training on **Pyrolysis Experiment and Synthesis of Carbon fibres from plant based precursors** at NSNRC for Nanotechnology and Bionanotechnology, Ambernath Maharashtra from 1st June to 30th June, 2010.
49. Participated in a refresher course on **Physics and Chemistry of Advanced Materials** at Academic Staff College, University of North Bengal, Darjeeling from 15th Nov, 2011 to 5th Dec, 2011.
50. Participated in a refresher course on **Physics and Chemistry of Advanced Materials** at Academic Staff College, University of North Bengal, Darjeeling from 21st Nov, 2011 to 11th Dec, 2012.
51. Resource lecture in the workshop on 'Recent Advances on Chemical Sciences and Technologies' at NIT, Silchar on 27th March, 2016.



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Catalyst free low temperature synthesis and antioxidant activity of multiwalled carbon nanotubes accessed from ghee, clarified butter of cow's milk

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ABSTRACT

Multiwalled carbon nanotubes (MWCNTs) have been synthesized at low temperature on silicon substrates in a thermal chemical vapor reactor from *ghee*, clarified butter from cow's milk as the carbon source without using any catalyst. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analyses revealed bundles of micrometer long MWCNTs with an interlayer separation of 0.33 nm consisting of 25 concentric graphene sheets with outer and inner diameters of 27.45 and 13.68 nm, respectively. The powder X-ray diffraction (XRD) pattern showed a hexagonal structure of graphitic carbon with average crystallite size of 4.6 nm. The MWCNTs exhibited pronounced antioxidant activity.

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1. Introduction

Since the discovery of multiwalled carbon nanotubes by Iijima in 1991 there is worldwide enthusiasm about carbon nanotubes (CNTs) and their unique properties enabled by their nanoscale structures spanning across academia and industry [1]. Of the number of synthetic techniques, chemical vapor deposition (CVD) is plausibly the most efficient method for the large scale production of CNTs [2–4]. The ability to grow nanotubes directly on substrate using CVD technique allows the fabrication of high purity nanotubes in a controlled manner. This method provides reasonably good perspectives on large-scale and low-cost processes for the mass production of CNTs, a key point for their application at the industrial scale. Fossil fuel based carbonaceous precursors such as methane, benzene, acetylene, ethanol, xylene etc. are being conventionally used as precursor for accessing CNTs [1–5]. Natural precursors such as camphor, turpentine, neem and eucalyptus oil are also documented for production of CNTs via a CVD method [5–8]. Recently, single-walled CNTs, MWCNTs and vertically aligned MWCNTs were accessed by this method using natural carbon feedstock [9–11]. Reports on the synthesis of CNTs from natural precursors are scant. Our attention has been drawn to animal derived fat as a potential source for the scalable production of

CNTs. Indian *ghee*, essentially a form of clarified butter obtained from cow's milk, is made by melting butter. Controlled synthesis of nanotubes thus unfolds newer possibilities particularly in the context of electromechanical properties and devices, chemical functionalization, surface chemistry, photochemistry, molecular sensors etc. [12]. CNTs, often perceived as rolled up graphene sheets, owing to large arrays of conjugated double bonds can readily scavenge free radicals. As opposed to a staggering number of papers dealing with CNTs those which involve antioxidant activity of such materials are extremely scarce. Amazingly, only a few publications till date addressed the antioxidant activity of CNTs [13,14]. Accordingly, we report herein a catalyst free low temperature synthesis of MWCNTs using Indian *ghee* derived from cow's milk and its free radical scavenging potential. Pertinent here is to mention that the carbon feedstock used herein is inexpensive and renewable green biosource for the production of CNTs.

2. Experimental

Materials and measurements: Clarified butter more commonly called *ghee* in India is pure butterfat left over after the milk solids and water are removed from butter (Fig. 1(a)). Like clarified butter, *ghee* is made by melting butter, cooking off the water and separating the clear, golden butter fat from the milk solids. Unlike commercially available butter, *ghee* in Indian tradition is simmered for a little while, thus browning the milk solids and adding a

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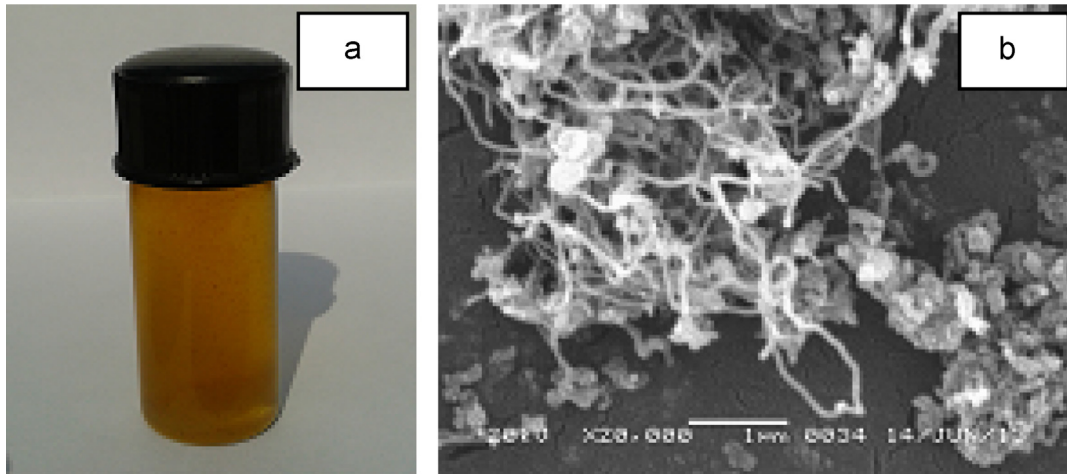


Fig. 1. (a) Digital image of clarified butter and (b) SEM image of MWCNT.

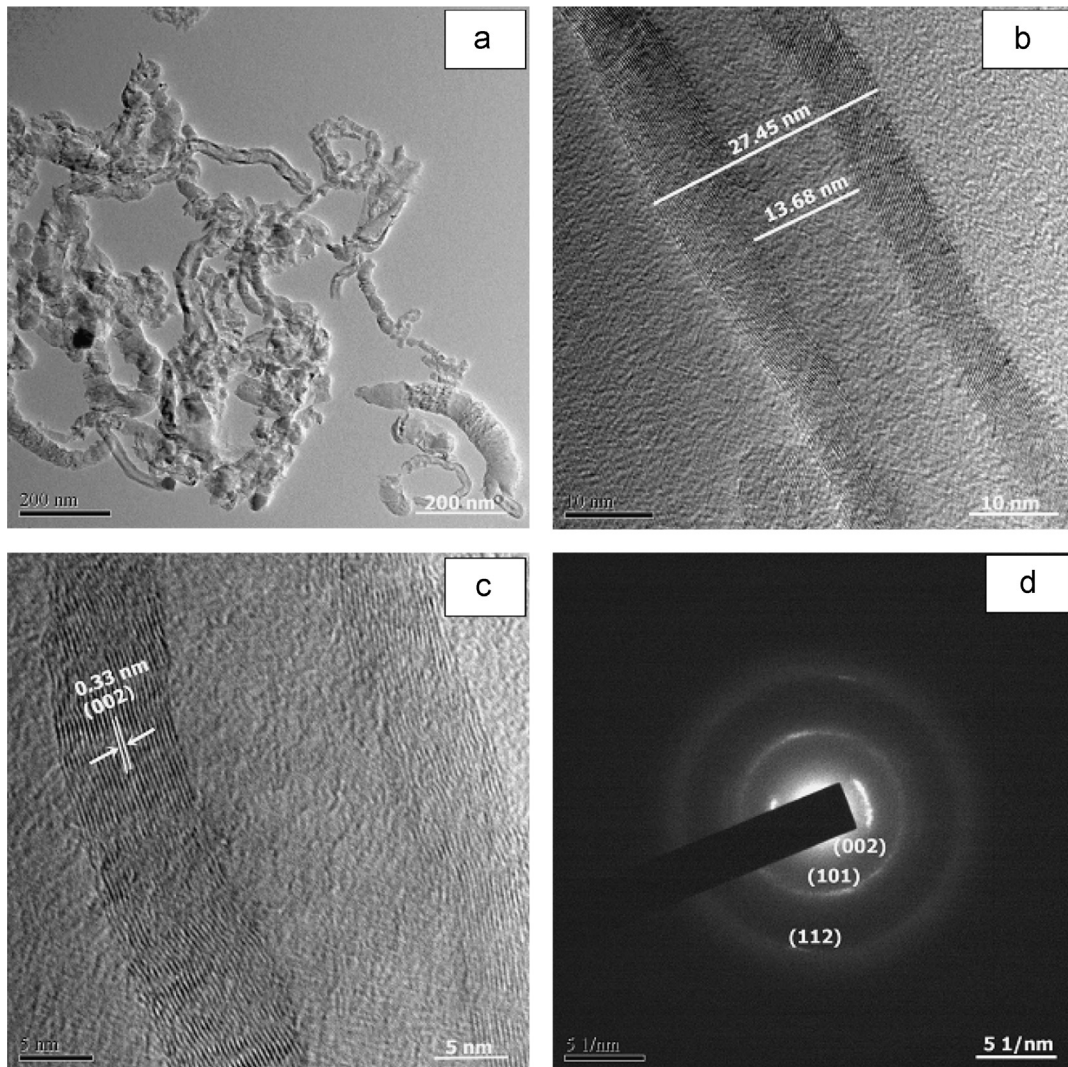


Fig. 2. (a) TEM image (b) and (c) HRTEM images and (d) ED pattern of MWCNT.

slightly nutty flavor to the finished product. *Ghee* has a smoke point of ~ 240 °C compared to 175 °C for ordinary butter. It has a longer shelf life and when stored in an airtight container can be

preserved at room temperature for years. The *ghee* used in the present work is obtained from cow's milk using traditional Indian procedure (*vide infra*).

Powder X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8-Advance diffractometer using the Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$) with a scan speed of $2^\circ/\text{min}$. TEM images were obtained on a JEM-2100, JEOL microscope. The samples were dispersed in ethanol under sonication and TEM grids were prepared using a few drops of the dispersion followed by drying in air. SEM images were obtained on a JEOL, JSM-6360 equipment. A Shimadzu 1601 PC UV–visible spectrophotometer was used to determine the variation in DPPH concentrations at 514 nm.

Synthesis of MWCNTs: The MWCNTs were prepared by the CVD method without using any catalyst. A quartz boat loaded with fresh ghee (10 g) was kept in a lower-temperature zone (300°C) and an empty quartz boat was kept at a higher temperature zone (750°C) in a horizontal quartz tube. Hydrogen gas was then purged at a rate of $6 \text{ cm}^3/\text{min}$. The furnace was heated to 750°C at a rate of $7^\circ\text{C}/\text{min}$ for 2 h and then allowed to cool to ambient temperature whereupon the CNTs were obtained as black powder (yield $\sim 3 \text{ g}$).

Assessment of antioxidant activity: The antioxidant activity of the MWCNTs were assessed using a modified 2,2-diphenyl-1-picrylhydrazyl, DPPH method [15]. An amount of 4 mg of the powdered MWCNTs sample was taken in a test tube and treated with 3 mL, $100 \mu\text{M}$ methanolic solution of DPPH. To enhance the surface reaction between the MWCNTs and the DPPH, the mixture was sonicated in the dark. The supernatant was collected by centrifugation and absorbance measured at 514 nm with DPPH as reference. The procedure was repeated at periodic interval of 15, 30, 45 and 60 min to ascertain time dependent DPPH scavenging [DPPH scavenging (%) = $\{(A_c - A_s)/A_c\} \times 100$]; A_c and A_s are absorbances of the control and MWCNTs. For evaluating SC50 (the amount of samples required to scavenge 50% of DPPH), a similar procedure is adopted with 2, 4, 6, 8, and 10 mg of MWCNTs and absorbances recorded after 30 min.

3. Results and discussion

The synthesized MWCNTs were characterized by SEM, TEM, and powder XRD studies. The SEM micrograph (Fig. 1(b)) revealed the presence of intertwined bundles of micrometer length CNTs.

The TEM micrographs (Fig. 2(a) and (b)) revealed the tubular structure of nanotubes. The HRTEM image (Fig. 2(c)) also suggested the as-grown nanotubes to be consisting of concentrically nested ~ 25 graphene sheets with the outer and inner diameters of 27.45 and 13.68 nm, respectively. The interlayer distance is about 0.33 nm which resembles that of (002) plane of the standard graphitic

carbon. The SAED pattern showed the concentric rings indicating polycrystalline nature of the material (Fig. 2(d)).

The powder XRD pattern of the synthesized MWCNTs is shown in Fig. 3. A number of strong Bragg reflections were obtained in the pattern corresponding to the (002), (100), (101) (102) and (004) reflections of hexagonal graphitic carbon (JCPDS Card no. 23-0064) possessing space group $P6_3/\text{mmc}$. The average crystallite size estimated by the Debye–Scherrer equation, $d = 0.9\lambda/\beta\cos\theta$ using a Gaussian fit was found to be 4.6 nm [16,17].

The antioxidant activity of the MWCNTs was studied in an *in vitro* system, using modified DPPH method as reported by Serpen et al. [15] for insoluble solid materials. The DPPH is a stable free radical for evaluating antioxidant potency of compounds. It is reduced by accepting the hydrogen or electron. The DPPH reducing ability of MWCNTs was assessed spectrophotometrically by observing color change from purple to yellow. The UV–visible absorption of DPPH is invariant of time. MWCNTs with DPPH added, however, showed a steady decrease in absorbance at 514 nm (Fig. 4(a)). The DPPH scavenging percentage was calculated corresponding to the quantity of DPPH in the methanolic solution. As evident from Fig. 4 (a), more than 50% and 70% of the DPPH were scavenged after 30 min and 60 min, respectively for 4 mg of the as-prepared MWCNTs. The SC50 value was ascertained graphically (Fig. 4(b)) to be 3.8 mg. The observed antioxidant activity is attributed to the

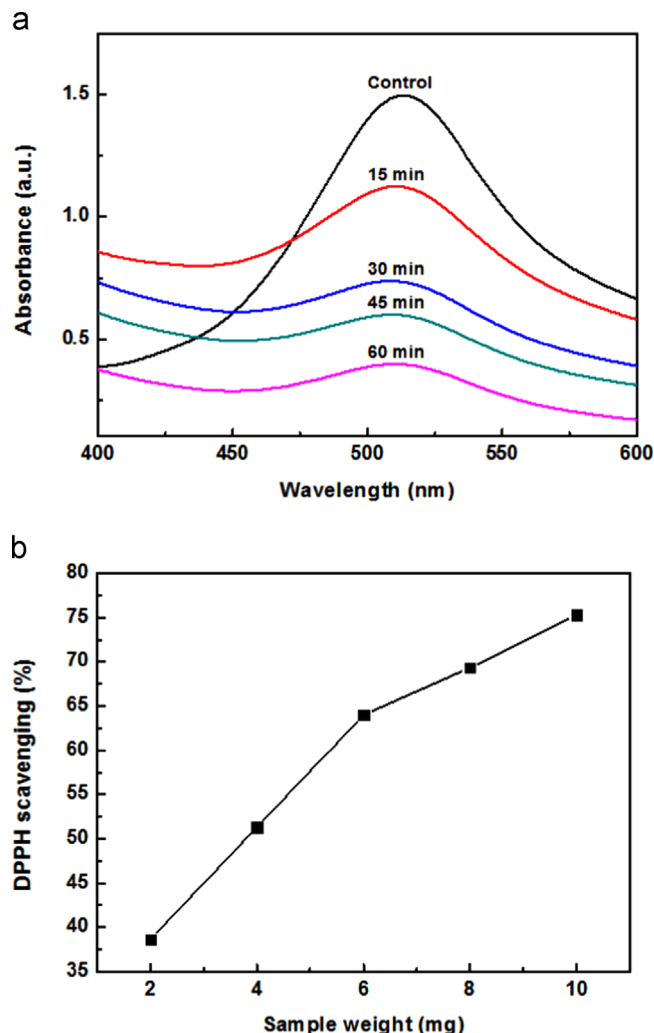


Fig. 3. XRD pattern of MWCNT.

Fig. 4. (a) Time dependent DPPH scavenging by MWCNT and (b) DPPH scavenging (%) at different weight of MWCNT.

neutralization of free radical character of DPPH by the transfer of an electron [18].

4. Conclusion

Multiwalled carbon nanotubes have been efficiently synthesized at low temperature from *ghee*, the clarified butter as the carbon source. The methodology adopted does not require any catalyst or pretreatment by toxic chemicals. The use of inexpensive renewable biosource, *ghee*, as precursor is anticipated to serve as a scalable 'green protocol' for production of MWCNTs. The as-prepared pristine MWCNTs showed significant free radical scavenging activity.

Acknowledgments

Authors thank Sophisticated Analytical Instrument Facility, North Eastern Hill University, Shillong and University Science Instrumentation Centre, Gauhati University, Guwahati for instrumental facilities.

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Green synthesis of novel antioxidant luminescent silica nanoparticle embedded carbon nanocomposites from a blue-green alga

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Abstract: Silica nanoparticle embedded carbon 2D-nanocomposite material has been synthesized using a green procedure from a blue green alga, *Scytonema guyanense*, by direct pyrolysis at 600°C under inert atmosphere. The nanocomposite was characterized by Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), powder X-ray diffraction and energy dispersive spectroscopy (EDS). Characteristic Si-O-Si vibrational absorptions at $\sim 720\text{ cm}^{-1}$, $\sim 790\text{ cm}^{-1}$ and $\sim 1080\text{ cm}^{-1}$ attested the occurrence of silica in the nanocomposite material. Transmission electron microscopy (TEM) analysis revealed five-fold multiply twinned quasi spherical silica nanoparticles ($\sim 40\text{ nm}$) embedded in $\sim 3\text{ nm}$ thick carbon nanoflakes. The material exhibited weak luminescence at 340 nm. The 2,2-diphenyl-1-picrylhydrazyl (DPPH) scavenging study showed moderate antioxidant activity of the material.

Keywords: antioxidant; blue-green alga; HRTEM; nanocomposites.

1 Introduction

Use of dried biomass, aqueous or organic extract of plants including lower forms such as fungi, algae and lichens, for accessing metal based nanoparticles has drawn wide interest of researchers [1–4] in the last

decade or so. Pyrolysis of plant based precursors to afford carbon nanomaterials, however, are only recently beginning to find sporadic attention [5]. Besides carbon nanomaterials, interests in carbon nanocomposite are rapidly growing [6, 7]. Strongly coupled hybrids of inorganic nanomaterials and novel graphitic nanocarbon materials such as carbon nanotubes and graphene represent a heuristic approach to synthesizing electrochemical energy storage materials. Inorganic nanocarbon hybrid materials have captured fascinating interests as high performance electrode materials than traditional counterparts made by simple physical mixing of electrochemically active inorganic element and conducting carbon materials. Nanocarbons with various degrees of oxidation provide a novel substrate for nanoparticle nucleation and growth [8]. While graphene, carbon nanotube and carbon nanofiber materials have recently earned a lot of attention as a viable alternative to replace activated carbon materials, the synthesis protocols are quite expensive. Due to the large specific capacity and low working potential, silicon is considered as a suitable candidate to substitute existing graphitic anodes. Electrodes made of pure silicon, however, have shown poor mechanical integrity and dramatic expansion of the material during battery operation, thus precluding their adoption [9]. The carbon-silicon nanocomposites, by contrast, provide excellent mechanical, electrochemical and electrical properties of carbon with the superior lithium intercalation ability of silicon. The manufacture of carbon-silicon composites for anodes by mechanical milling has been explored [10]. A new class of silica-carbon nanocomposites has recently been employed as solid catalyst for cellulose hydrolysis that yielded high glucose compared to reference catalysts and commercial zeolites [11]. It is believed that the organic part of the composite material offers flexibility and versatility for further functionalization, while the silica component renders mechanical and thermal stability. To ensure high entanglement of carbon and silica in the nanocomposite, an evaporation-induced triconstituent co-assembly method was explored [12]. Besides nanoparticle size and composition, particle shape also plays a crucial role in achieving

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different applications. Several chemical routes which were explored to prepare carbon-silica hybrid materials from different carbon and silicon based precursors are complicated, often expensive and based on toxic carbon or silicon source [13, 14]. Rice husk has been extensively worked upon to afford carbon-silicon material. Reviews by Lee and Cutler [15] and a very recent one by Chiew and Cheong [16] dealt with carbon-silicon material from plant based biomass. Although synthesis of C-Si composite material from biomass is marred with problems of low yield and impurities, the renewable and abundant plant biomass provide a viable option for consideration. The cellulosic component in these plant-based biomasses can be readily converted to carbon with lot of silica getting accumulated at the outer epidermis [17]. This leads to intimate contact between carbon content and silica generating a high surface area by the nanoparticle [18, 19]. In this paper, we report a renewable and scalable green protocol for accessing carbon-silica hybrid nanomaterial from inexpensive algal biomass. This is believed to be the first example of carbon-silica nanocomposite being accessed from plant based biomass.

2 Materials and methods

2.1 Materials and measurements

The alga, Figure 1A, was collected from the exposed surfaces (concrete substratum) of the departmental building in Assam University campus, located near Silchar town (Assam), India. Based on morphological characteristics, the species has been identified following standard keys to be *Scytonema guyanense* var. *minus*, a blue green alga [20]. It is found to grow luxuriantly on stony surfaces forming thick mats during the rainy season. The sample was thoroughly washed with distilled water to remove any dirt, shade dried, ground to powder in a glass mortar and used as such.

X-ray diffraction measurements were carried out on a Philips X'PERT powder X-ray diffractometer (Almelo, Netherland) using the Cu-K α radiation ($\lambda=1.54056$ Å) with a scan speed 2°/min. Transmission electron microscopy (TEM) images were obtained on a JEM-2100, JEOL equipment (Tokyo, Japan). The TEM grids were prepared using a few of drops of the ethanol dispersed powder. The scanning electron microscopy (SEM) images were recorded on a JEOL, JSM-6360 microscope (Tokyo, Japan) with energy dispersive spectroscopy (EDS) attachment. Fourier transform infrared (FT-IR) spectrum of the material was recorded on a Perkin Elmer spectrum 2 spectrophotometer (Billerica, MA, USA) using KBr pellets. A Shimadzu 1601PC UV-visible spectrophotometer was used to record optical behavior of the nanomaterial and monitor the extent of diphenyl-1-picrylhydrazyl (DPPH, Sigma-Aldrich, Bengaluru, India) scavenging. Photoluminescence spectrum was recorded on a Shimadzu RF-5301 PC spectrofluorophotometer (Kyoto, Japan).

2.2 Carbon-silica nanocomposite

The production of carbon-silica nanocomposite from algal (*Scytonema sp.*) biomass was carried out by direct pyrolysis under inert conditions. The dried algal biomass (10 g) taken in a quartz tube was heated to 600°C in a chemical vapor deposition chamber at a heating rate of 7°C/min for 2 h under an argon flow rate of 6 cm³/min, to afford a black powder. The yield recorded was 2.8 g (~30%).

2.3 Antioxidant activity

The antioxidant activity of the nanocomposite was assessed using a modified DPPH method [21]. An amount of 4 mg powdered sample was taken in a test tube and treated with 3 ml, 100 μ M methanolic solution of DPPH. The mixture was sonicated in the dark for 15 min to enhance the surface reaction between the nanocomposite material and the DPPH. The optical absorptions of the supernatant were monitored at 517 nm with DPPH as reference at periodic intervals of 15 min, 30 min, 45 min and 60 min to ascertain time dependent DPPH scavenging. For evaluating SC-50 (the amount required to scavenge 50% of DPPH free radicals), a similar procedure was adopted for 2 mg, 4 mg, 6 mg, 8 mg, 10 mg and 15 mg of the material and absorbances recorded after 30 min.

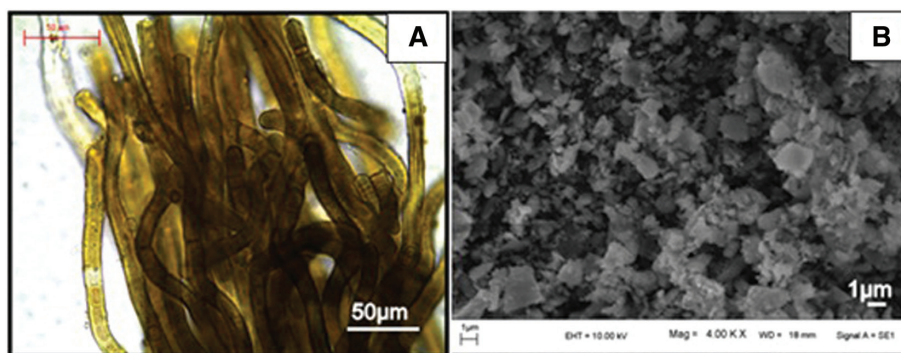
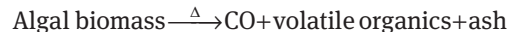


Figure 1: Algae and nanocomposite. (A) Optical microscopic image of *Scytonema guyanense* var. *minus* and (B) scanning electron microscopy (SEM) image.

3 Results and discussion

The algal biomass afforded the carbon-silica nanocomposite in relatively good yield considering that most of the algal biomass volatilized off at the experimental temperature. The synthesis was carried out using the algal biomass as a precursor simply by direct pyrolysis under inert atmosphere and no other reagents were used for pretreatments. At a temperature below $\sim 600^\circ\text{C}$ or so and holding time < 2 h, the pyrolysis was found to be incomplete as the material obtained was agglomerated with a lot of extraneous matter. Organic compounds in plant biomass tend to decompose at $\sim 400^\circ\text{C}$ and cellulose decomposition and the cleavage of bonds of organic molecules to silicon usually takes place at $\sim 550^\circ\text{C}$ [22]. A higher temperature (up to 700°C) and holding time of pyrolysis (up to 4 h) did not appreciably alter the morphology or yield of the material. Thus the temperature of 600°C and a holding time of 2 h were set as optimum conditions to gain access to the nanocomposite. It is pertinent to mention herein that besides such carbonization methods, multicomponent co-assembly processes have also recently begun to attract the fancy of researchers to afford carbon-silica

nanocomposites [23, 24]. The chemical reaction involved in the present pyrolytic process may be represented by:



The ash residue is the carbonized silica. In oxidative treatment, a similar pathway is believed to be involved with CO_2 being an additional product [25]. The filamentous alga, *Scytonema sp.* used herein has been a source of homogeneous chemical raw material for the production of C-Si nanocomposites.

The scanning electron microscopy (SEM) micrograph showed a flake type morphology with spherical particles embedded (Figure 1B).

The TEM micrographs (Figures 2A and 2B) revealed the presence of silica nanoparticles of nonuniform sizes embedded in carbon nanoflakes. The thicknesses of the flakes are ~ 3 nm. The high resolution TEM (HRTEM) micrographs (Figure 2C) showed silica nanoparticles to be quasi-spherical five-fold multiply twinned. The 0.18 nm interplanar distance of lattice fringes corresponds to $11\bar{2}$ plane of silica. Circular rings typical of graphitic carbon and scattered spots originating from embedded silica nanoparticles are both visible in the selected area electron

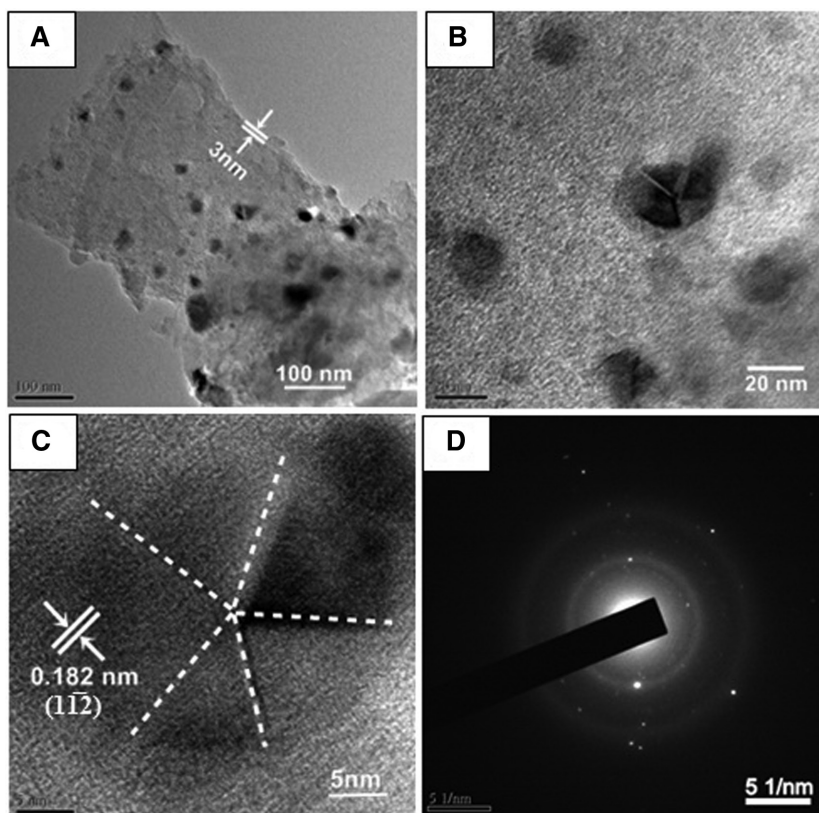


Figure 2: Electron microscopy of nanocomposite. (A, B) transmission electron microscopy (TEM) image, (C) high resolution transmission electron microscopy (HRTEM) image and (D) electron diffraction pattern.

diffraction profile (Figure 2D). The size of the embedded silica nanoparticles (Figure 2C) as revealed from HRTEM ranged from 25 nm to 40 nm.

The EDS analysis (Figure 3A) revealed the occurrence of carbon, oxygen and silicon as the major constituents.

The X-ray diffraction spectrum (Figure 3B) is replete with a rather large number of peaks ($2\theta \sim 10^\circ$ to 80°); some correspond to the crystallographic planes of hexagonal silicon dioxide (Joint Committee on Powder Diffraction Standards [JCPDS] file no. 85-0504) while others relate to hexagonal graphitic carbon (JCPDS file no. 23-0064).

The average crystallite size (~ 41 nm) obtained using a Gaussian fit following the Debye-Scherrer method is compatible with that obtained from a TEM study.

The FT-IR spectrum (Figure 3C) exhibited diagnostic features at 720 cm^{-1} for the vibrational mode ($\nu_{\text{Si-O-Si}+\rho_{\text{CH}_2}}$), 790 cm^{-1} for the combination band ($\nu_{\text{Si-C}+\rho_{\text{a(CH}_3)}}$) and at 1080 cm^{-1} attributable to ($\nu_{\text{s Si-O-Si}}$) [26]. A relatively strong band at 1430 cm^{-1} is presumed to be associated with CH_2 deformation mode of graphitic carbon matrix. A rather weak and broad band at 3650 cm^{-1} was assigned to -OH function which may be attributed to surface adsorbed water [27].

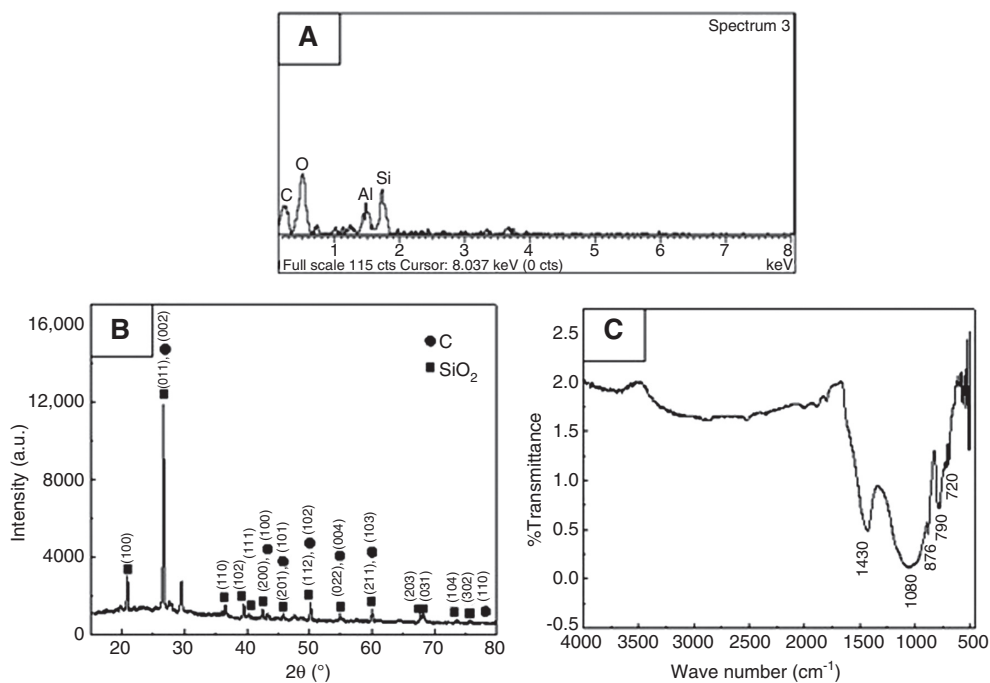


Figure 3: Spectra of nanocomposite. (A) Energy dispersive spectrum (EDS), (B) powder X-ray diffractogram (PXRD) and (C) Fourier transform infrared (FT-IR) spectrum.

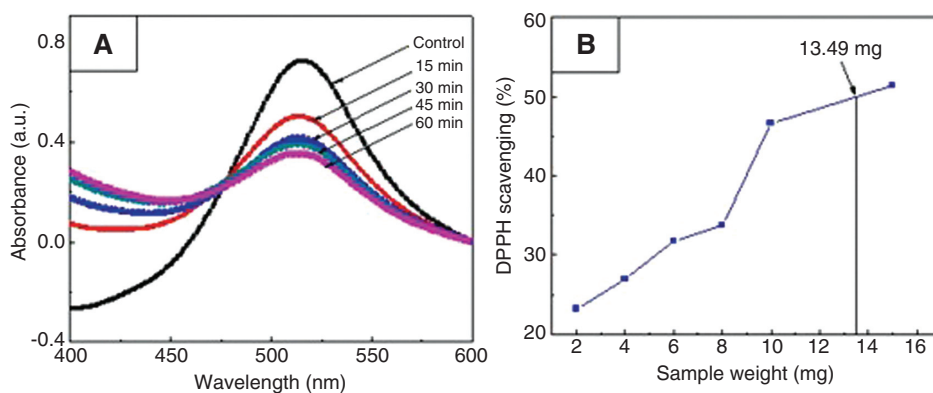


Figure 4: Antioxidant activity. (A) Time dependent diphenyl-1-picrylhydrazyl (DPPH) scavenging and (B) DPPH scavenging (%) at different weights of nanocomposite.

The material is fluorescent, showing a broad emission at 340 nm at an excitation wavelength of 240 nm. It is pertinent to mention that a lot of interest exists in the fluorescence property of nontoxic, biocompatible carbon-silica nanocomposites that are of relevance to bioimaging and bioanalytical applications [28, 29]. Although some reports on carbon nanotube-nanosilica are documented, photoluminescence properties of carbon-silica nanocomposite have not received much attention until now [30].

The antioxidant activity of the nanocomposite was studied *in vitro* using a modified DPPH method for insoluble solids [21] by UV-visible spectroscopy noting the color change from purple to yellow. The nanocomposite with DPPH added, showed a decline in absorbance at 517 nm (Figure 4A). About 50% of DPPH was scavenged after 1 h for 15 mg of the material with the SC-50 value ascertained to be 13.5 mg (Figures 4A and 4B). It may be mentioned that the free radical scavenging capacity of nanosilica-gallic acid as a nanoantioxidant is also well recognized [31, 32].

4 Conclusion

Novel carbon-silica nanocomposite materials have been synthesized from algal biomass as the abundant carbon source using a green protocol. The methodology adopted did not require any catalyst, pretreatment using toxic chemicals or complicated work-up procedure and is anticipated to serve as a low-cost, scalable option for production of carbon-silica nanocomposites. The alga *Scytonema guyanense* used for the synthesis is fast growing and readily isolable, thus serving as a renewable feedstock for the production of the nanocomposite. There is lot of scope for fine tuning the synthesis so as to improve the purity and reduce surface defects. The as-prepared pristine material showed moderate fluorescence and free radical scavenging activity and could be significant as an efficient catalyst, in high performance electrochemical anodes and in bioanalytical applications.

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Bionotes



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Graphical abstract

Abhijit Nath, Aparajita Das,
Shoubhonik Deb,
Chira R. Bhattacharjee and
Jayashree Rout

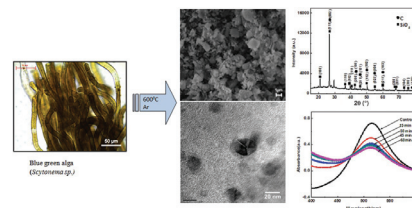
**Green synthesis of novel
antioxidant luminescent silica
nanoparticle embedded carbon
nanocomposites from a blue-green
alga**

DOI 10.1515/gps-2015-0124

Green Process Synth 2016; x: xxx–xxx

Original article: Novel carbon-silica nanocomposite exhibiting fluorescent and antioxidant activity has been accessed via a scalable green protocol from a renewable feedstock, blue-green alga, *Scytonema guyanense* var. *minus*.

Keywords: antioxidant; blue-green alga; HRTEM; nanocomposites.



Communication

Synthesis, X-ray Diffraction Study and Antimicrobial Activity of Calcium Sulphate Nanocomposites from Plant Charcoal

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Abstract: Calcium sulphate nanocomposite materials (CB) have been synthesised from plant charcoal. Crushed charcoal powder was heated to red hot over a Bunsen burner flame and produced a white material which has been isolated. The surface morphology of the material has been studied by Scanning Electron Microscopy (SEM) and the elements were analyzed by Energy Dispersion Spectroscopy (EDS). To explore the structural features of the materials X-Ray Diffraction (XRD) patterns were recorded. The material showed pronounced inhibitory effects against *Streptococcus faecalis*, *Bacillus subtilis*, *Klebsilla pneumoni*, *E. coli*, *Proteus vulgaris* and *Pseudomonas aeruginosa*.

Keywords: Charcoal, nanocomposite; XRD; antimicrobial activity.

1. Introduction

Despite the development of a variety of approaches for the synthesis of nanomaterials [1,2], production of such materials in commercial volumes at viable market prices is yet a challenging task. For the preparation of nanomaterials from carbonaceous sources subjecting the starting material to high temperatures has been a common approach. The vapourised material, which is rich in materials in the nano domain, is condensed and collected. Most often, not much attention is paid to the leftover solid residue. In this work, our focus was to study that nonvolatile leftover solid residue from charcoal. Charcoal is made by charring wood in the absence of air [3].

In normal wood ash, the major component is calcium carbonate [4]. Mishra and co-workers reported a very good account of wood ash composition as the function of furnace temperature [5]. They reported the presence of CaCO_3 , $\text{K}_2\text{Ca}(\text{CO}_3)_2$, $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ at 600 °C and CaO , MgO and Ca_2SiO at 1,300 °C. Ferrez and co-workers reported the synthesis of nano-hydroxyapatite microsphere (75-106 μm) by the treatment of calcium hydroxide with orthophosphoric acid and their potential as a delivery system for antibiotics [6]. A number of inorganic salts including calcium sulphate, calcium carbonate, copper carbonate etc, when used as additives, have been reported to enhance efficacy of *Beauveria bassiana* and *Metarhizium anisopliae* against the potato tuber moth *Phthorimaea operculella* (Zeller) [7].

We report herein the nano-structured inorganic nanocomposite material, CaSO_4 obtained from such charcoal-remainings and its antimicrobial properties. CaSO_4 is well known for its binding and adsorption activity. The presence of Ca^{2+} can influence the deposition of sulfate functionalized latex microspheres of natural organic matter [8]. The effect of particle size and natural organic matter on the latex particles migration in saturated porous media was studied by Pelley and Tufenkji [9]. Southam and his coworkers successfully utilized nanostructured calcium silicate for chemisorption of all forms of orthophosphate from aqueous solution [10,11]. Nanostructured calcium silicate consisting of nanometer-sized platelets arranged in particles (0.5 and 20 μm in size) seems to be efficient for treatment of aqueous waste containing phosphate and other ions [11]

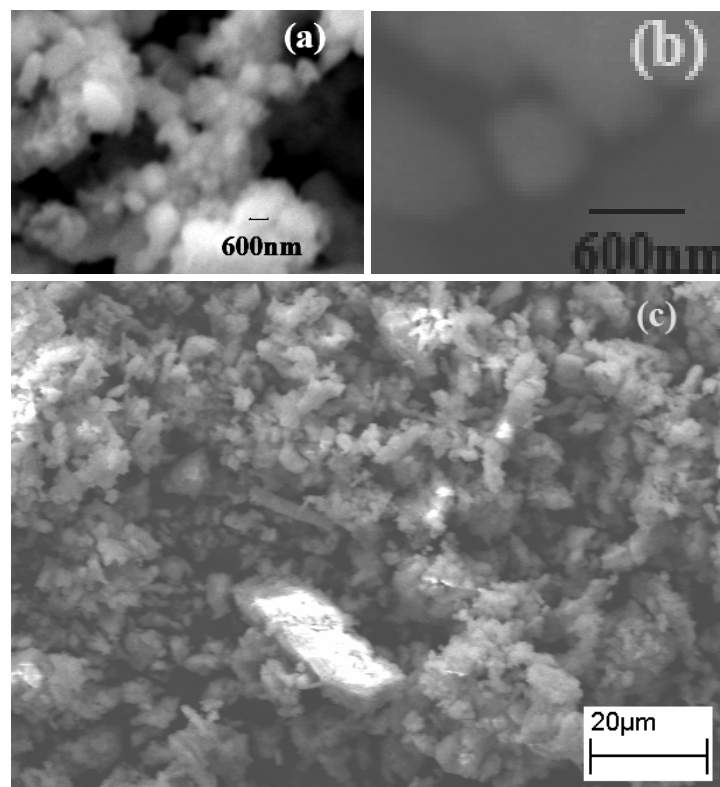
2. Results and Discussion

The material (coded as CB) was prepared as a white powder residue from the heating of plant charcoal to a red hot state. The white powder was used 'as obtained' (see Section 3.1). The morphology of the material was studied using Scanning Electron Microscopy (SEM) and analyzed in regards to its elemental composition by Energy Dispersive Spectroscopy (EDS). The antimicrobial activity of the material was studied by monitoring the zone of inhibition in sterile Muller Hinton agar, cooled to 45 °C.

2.1. SEM Studies

The SEM images show the presence of spherical nano-scaled domains forming micro-scale aggregates (Figure 1). The size of the spherical particle has been evaluated to be ~600 nm.

Figure 1. (a) Scanning Electron Microscopy (SEM) images of the synthesized material, CB; (b) single particles; (c) lower resolution image showing aggregates of CB.



2.2. Elemental Analysis

Energy Dispersion Spectroscopy (EDS) was performed to analyse the elemental composition. The study revealed the presence of oxygen, sulphur and calcium as the major constituents, along with minor contributions from sodium, magnesium, aluminium, silicon, chlorine, potassium and iron. The nitrogen content in wood ash is normally insignificant due to the conversion of most of the wood nitrogen to NH_3 , NO_x and N_2 during the combustion of wood [5]. The percentage composition is given in Table 1 and the EDS spectrum is displayed in the Figure 2.

Figure 2. EDS spectrum of the synthesized material, CB.

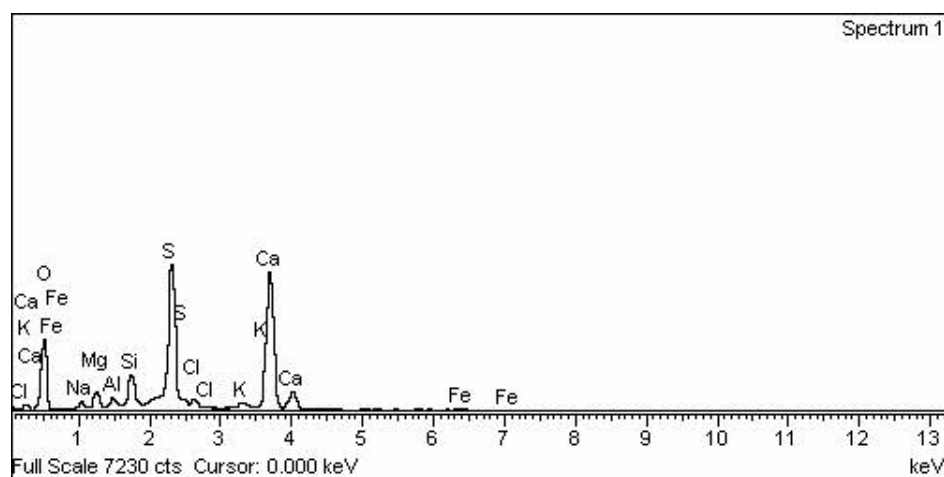


Table 1. Elemental composition of the material CB.

Element	App Conc.	Intensity	Weight%	Weight% Sigma	Atomic%
O	37.55	0.4370	49.94	0.78	68.23
Na	1.55	0.6542	1.38	0.18	1.31
Mg	2.30	0.6318	2.12	0.15	1.90
Al	1.13	0.7350	0.89	0.11	0.72
Si	4.65	0.8396	3.22	0.15	2.50
S	25.86	0.9334	16.10	0.34	10.97
Cl	1.49	0.7180	1.21	0.12	0.75
K	1.27	1.0228	0.72	0.10	0.40
Ca	39.14	0.9582	23.74	0.43	12.94
Fe	0.95	0.8093	0.68	0.15	0.27
Total			100.00		

2.3. XRD Studies

The X-Ray diffraction (XRD) pattern of the material is presented in Figure 3. The XRD pattern (and the data from EDS study) of the sample indicated the material to be mainly the CaSO₄ phase. The EDS studies indicated the atomic ratio of calcium and sulphur to be approximately 1:1, along with a high percentage of oxygen. The structure was tried to be resolved from the powder pattern using WinGX suit [12]. The pattern was found to show high similarity with the powder pattern simulated from the single crystal data of CaSO₄ with space group *A m m a* [13,14] using Mercury 1.4.1 suit [15]. Both the peak position and the intensity ratio exhibited a close match. The experimental (with corresponding Miller Indices) and the simulated patterns are presented in Figure 3 for comparison. The presence of the CaSO₄ phase also explains the high percentage of oxygen. The rest amount of oxygen seems to arise from other minor metal oxides, which are responsible for the minor extra reflections in the pattern (the unindexed reflections at 27 and at 39.5 [20]). No detectable evidence of the presence of CaO was found in the XRD pattern of the sample.

2.4. Study of Antimicrobial Activity

The activity of the material against different microorganisms was monitored with the as prepared sample. Disc diffusion method was used to determine the zone of inhibition. The material exhibited a very good inhibitory effect against *Streptococcus faecalis* and *Bacillus subtilis* and lesser activity against *Klebsilla pneumoniae*, *E. coli*, *Proteus vulgaris* and *Pseudomonas aeruginosa* relative to standards ciprofloxacin and clotrimazole (Table 2). The solvent chloroform has no antimicrobial activity as such. The antimicrobial property of the material seems to arise due to changes in the microenvironment in the vicinity of organism-particle contact area causing damage to the cell membranes on intimate contact between the cell and particle [16].

Figure 3. X-Ray diffraction (XRD) pattern of the material, CB. At the top the experimental (red) and the bottom the simulated powder pattern (blue) for CaSO_4 are plotted.

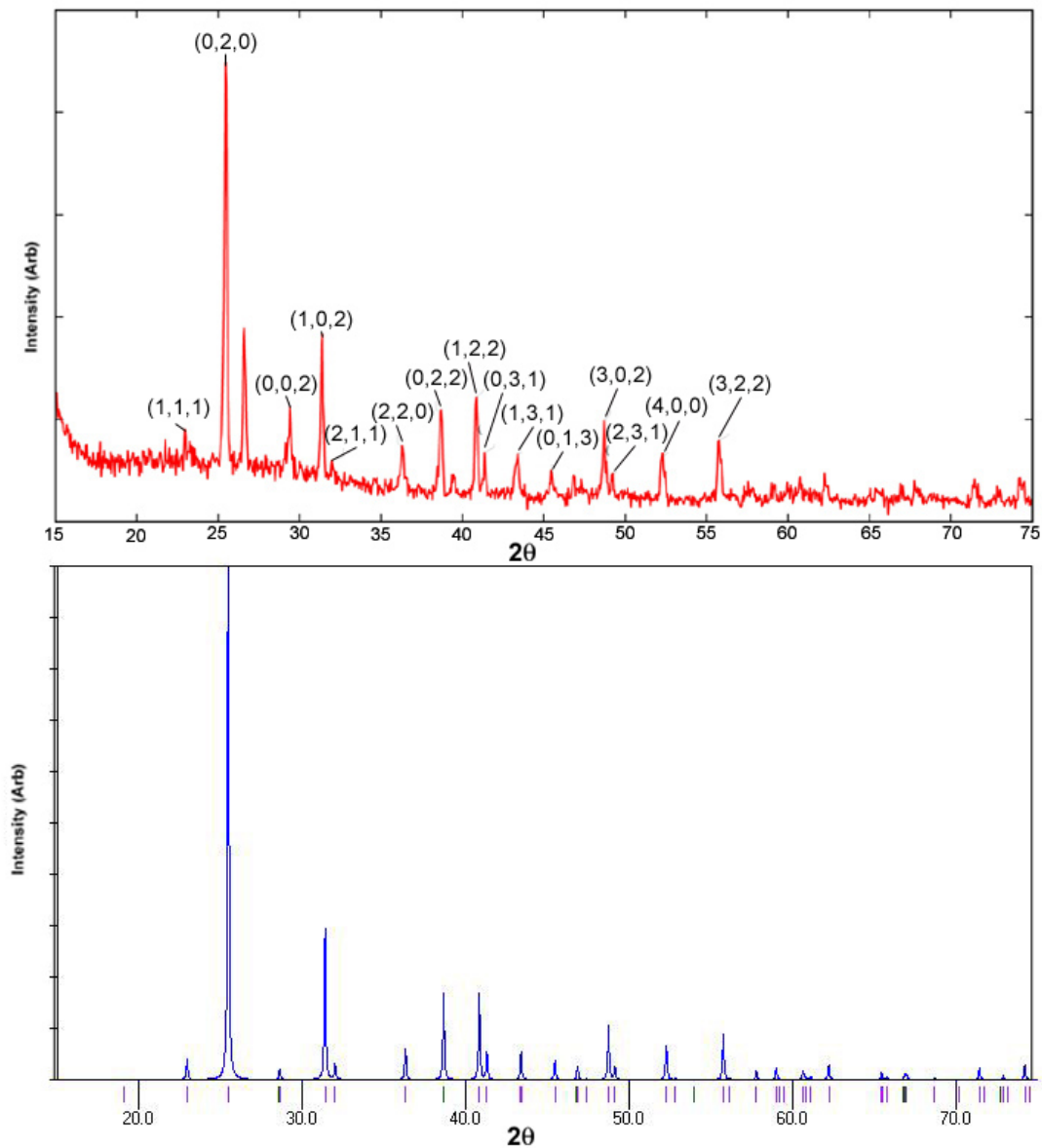


Table 2. Antimicrobial activity of the material CB.

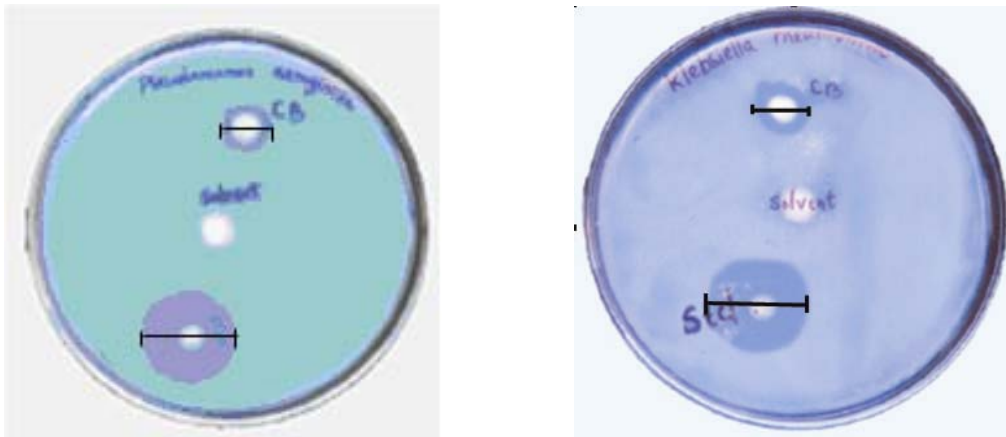
SI No.	Microbe	Standard (Zone of inhibition)	Solvent (CHCl_3)	CB (Zone of inhibition)
1	<i>Streptococcus faecalis</i>	40 mm	Nil	18 mm
2	<i>Bacillus subtilis</i>	32 mm	Nil	20 mm
3	<i>Klebsilla pneumoni</i>	30 mm	Nil	12 mm
4	<i>E. coli</i>	35 mm	Nil	13 mm
5	<i>Proteus vulgaris</i>	40 mm	Nil	12 mm
6	<i>Pseudomonas aeruginosa</i>	30 mm	Nil	12 mm

Standards used: Ciprofloxacin 10 $\mu\text{g}/\text{disc}$, Clotrimazole 10 $\mu\text{g}/\text{disc}$.

Figure 4. Photographs of two culture plates (the zone of inhibition is marked).

(a) [*Pseudomonas aeruginosa*]

(b) [*Klebsilla pneumoni*]



3. Experimental Section

3.1. Preparation of the materials

A block of plant charcoal (approx. 1.5 g), finely crushed into powder, was heated over a Bunsen burner flame to red hot for two hours. Carbon and other volatile oxidisable materials were removed under these conditions. A white powder residue remained after heat treatment, which was analyzed 'as obtained'. The morphology of the material was studied using Scanning Electron Microscopy and Energy Dispersive Spectroscopy. The antimicrobial activity of the material was studied by monitoring the zone of inhibition in sterile Muller Hinton agar, cooled to 45 °C

3.2. Study of antimicrobial activity

The disc diffusion method was used to determine the inhibition zones. Sterile molten Muller & Hynton agar cooled to 45°C was inoculated with different organisms. The inoculums used were the young cultures and the inoculum size was standardized in such a way that each mL contains 10⁸ cells. Using an aseptic technique the inoculum was uniformly inoculated over the molten agar with sterile cotton swabs. A Watmann No 2 filter paper disc of 6 mm diameter containing 200 µL/disc of sample was placed over the inoculated medium. The plates were allowed to remain at room temperature for two hours. Then the plates were incubated at 37°C for 24 hours. The zone of inhibition was measured using a Zone Reader.

3.3. X-Ray Diffraction (XRD) Study

A capillary filled with the sample was used for XRD studies. The powder was finely ground to ensure random orientation of the crystals so that there are detectable signals at all angles and that the background noise is kept to a minimum. The samples were analyzed using a copper target to generate X-rays of 0.154 nm wavelength.

4. Conclusions

In conclusion, we have prepared calcium sulphate nanocomposite antimicrobial materials from the nonvolatile fraction of charcoal in an inexpensive way and evaluated their activity against a number of microorganisms. As the materials, *as prepared*, exhibited good microbial inhibitory effect, a more focused effect may be obtained by functionalizing the surface of the material particles. Currently the evaluation of the composite materials as drug carrier is in progress.

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Research Article

Synthesis and Characterization of Carbon Nanotubes Using a Natural Precursor: Turpentine Oil

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Abstract

Pure Carbon nanotubes (CNTs) have been efficiently synthesized from Turpentine oil using Fe nanoparticles as a catalyst and also without the use of catalyst by simple Chemical Vapour Deposition (CVD) method at 900 °C. Turpentine oil (C₁₀H₁₆), a plant-based precursor was used as a source of carbon and argon as a carrier gas. The CNTs have been grown directly inside the quartz tube. The as grown carbon nanotubes were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X- Ray diffraction (XRD) studies. The XRD data indicated the presence of a high degree of crystallinity and the graphitic nature of the synthesized tubes. These tubes have been found to have outer diameters between 12 and 15 nm.

Keywords: Carbon nano tubes, Chemical vapour deposition, Catalyst.

1. Introduction

During the past few years, carbon nanotubes have attracted much attention because of their unique physico-chemical and mechanical properties [1,2], as well as the potential applications such as in electron field emitters, biosensors, electrode material for solar cells, fuel cells and so on [3-7]. Carbon nanotubes

as light-weight and high performance materials are expected to bring major changes in the automobile sector by replacing steel or aluminum body and in the medicine area as a smart drug deliver [8].

From the application point of view it is highly desirable to synthesize well-ordered arrays of nanotubes at low cost.

In general, carbon nanotubes are mainly synthesized by arc discharge, laser ablation, and chemical vapor deposition method [9–11]. Compared with other methods, chemical vapor deposition (CVD) is a very effective technique because of low cost production, controllability, and the viability in highly dense synthesis of nanotubes at lower temperature on various substrates [12,13]. Recently, vertically aligned carbon nanotubes [14], multiwalled carbon nanotubes [15], and single-walled carbon nanotubes [16] were synthesized by this simple method using natural precursor as a carbon feedstock. The advantage of the natural precursors over conventional precursors (methane, acetylene, alcohol, benzene, etc.) lies in the reproducibility [14–16]. So far, there have been few reports about the synthesis of carbon nanotubes from natural precursors. In the present investigation, attempts were made to prepare the carbon nanotubes using turpentine oil as a carbon feedstock.

2. Materials and Methods

The synthesis of CNTs was carried out using the CVD method. The process involved pyrolytic degradation of oil at suitable temperatures and atmosphere free from oxygen. Turpentine oil, derivable from the resin of pine trees, used as the carbon source has a purity of ~99.5% (Sigma Aldrich). Fe nanoparticles were used as catalyst to grow the CNTs. The Fe nano particles were synthesized from analytical-grade ferric nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma Aldrich). A quartz boat loaded with oil was kept in a lower-temperature zone while the catalyst particles in another boat at a higher-temperature zone of a horizontal quartz tube (1m long with an inner diameter of 25 mm) in a dual-zone furnace (300 mm long). The outer part of the quartz tube was attached with a water bubbler. The reaction parameters such as argon (Ar) gas and its flow rate, temperature, and duration of heating, were set per requirement. In a typical experiment, the horizontal quartz tube containing quartz boats was first flushed with Ar gas in order to eliminate air from the tube.

Then the gas was allowed to flow with a flow rate of 6 ml/min. The furnace was then switched on to attain the set temperature of 900 °C at a rate of 7 °C /min. When the desired temperature was reached, the furnace was left on for a set duration of 3 hours and then allowed to cool down to room temperature under the Ar gas flow.

After cooling, the carbon materials were taken out and powdered, then weighed to calculate the yield.

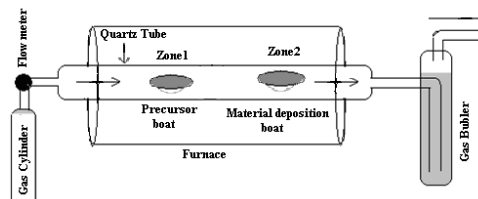
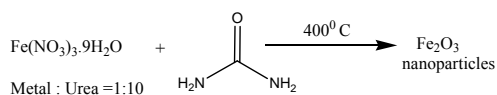
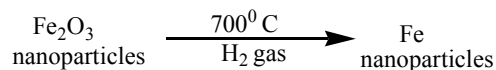


Figure 1. A self explanatory schematic diagram of pyrolysing unit used for preparation of carbon materials from turpentine oil.

Synthesis of Catalyst. In a typical method of synthesis, the solutions of ferric nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and urea were prepared separately in deionized water keeping the molar ratio at 1:10. Then the two solutions were mixed in a beaker and stirred with a magnetic stirrer at room temperature until a homogeneous solution was obtained. The mixed solution was then transferred into a round-bottomed flask, and the flask was sealed and heated to a temperature of 400°C for 1.5 hours. Upon completion of the reaction, the product was washed with deionized water till it was neutral, to remove the possible absorbed ions and chemicals in order to inhibit agglomeration. The resulted precipitate, in the form of metal hydroxide, was dried and calcined in at 400°C for 1 hour to obtain Fe_2O_3 nanoparticles. The synthesized Fe_2O_3 nano particles were then reduced in a H_2 gas environment at 700°C for 2 hours in a CVD apparatus. The schematic of the synthesis is represented as the following:



Step 1. Synthesis of Fe_2O_3 nano particles



Step 2. Reduction of Fe_2O_3 nano particles

Characterization of the CNTs. Powder X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer using the $\text{Cu-K}\alpha$ radiation ($\lambda=1.5418\text{\AA}$) with a scan speed $2^\circ/\text{min}$. Transmission electron microscopy images were obtained on a JEOL, 9JSM-100CX transmission electron microscope (TEM) with an accelerating voltage of 100kV. The sample powders were dispersed in ethanol, under sonication and TEM grids were prepared using a few of drops of the dispersion followed by drying in air. Scanning electron microscopy (SEM) images were obtained on a JEOL, JSM scanning electron microscope (SEM).

3. Results and Discussion

The yield of the carbon materials was found to be in the range of 30-33%. The densities of the carbon synthesized from turpentine oil with or without the catalyst were in the range of 0.21 to 0.26. The results show that the density of the synthesized materials is much lower than that of the graphitic carbon and amorphous carbon [17]. The morphology and internal structure of the synthesized carbon materials were investigated through the SEM and TEM studies.

Turpentine oil on pyrolysis at 900°C in presence of Fe nanoparticles as catalyst produced tubes of 12-15 nm in diameters while the unanalyzed reaction yielded tubes of 20-30 nm in diameter. The important

distinction between the catalyzed and uncatalyzed carbon formation is in the uncatalyzed reaction which exhibited the formation of CNT along with amorphous carbon, whereas the reactions using Fe as catalyst formed less amorphous carbon as almost pure nano tubes are formed (Figures 5(a) and 5(b)).

SEM Studies. The SEM micrograph of the carbon material derived from turpentine oil using Fe nanoparticles as catalyst was shown in the Figure 2. The image shows the possible existence of carbon nanotubes.

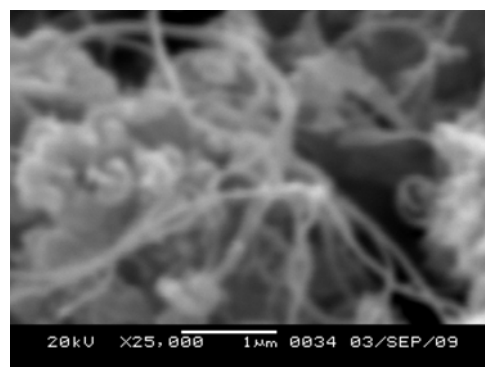


Figure 2. SEM micrographs of carbon obtained from catalyzed reaction.

TEM Studies. The TEM micrographs of the CNTs synthesized by catalytic CVD of turpentine oil using

Fe nanoparticles as nucleating agent are presented in Figures 3(a) and 3(b). The diameters of the tubes were recorded in the range of 12-15 nm. The TEM images of the carbon obtained from unanalyzed reactions also indicate the presence of branched CNTs (Fig.4a and 4b) having diameters in the range of 20-30 nm. The TEM micrographs given in Figures 5(a) and 5(b) indicate the presence of Fe nano particles. The particles are less dispersed and show agglomeration with dimension was in the range 30-35 nm.

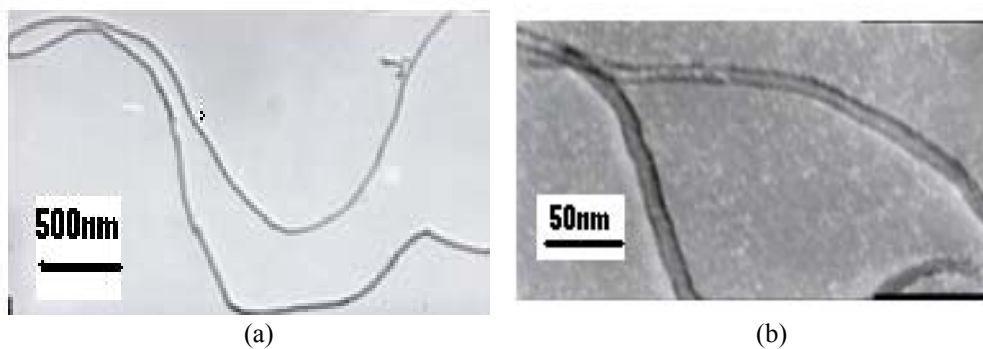


Figure 3. TEM micrographs of carbon from catalysed reaction of turpentine oil (a) scale 500 nm (b) scale 50 nm.

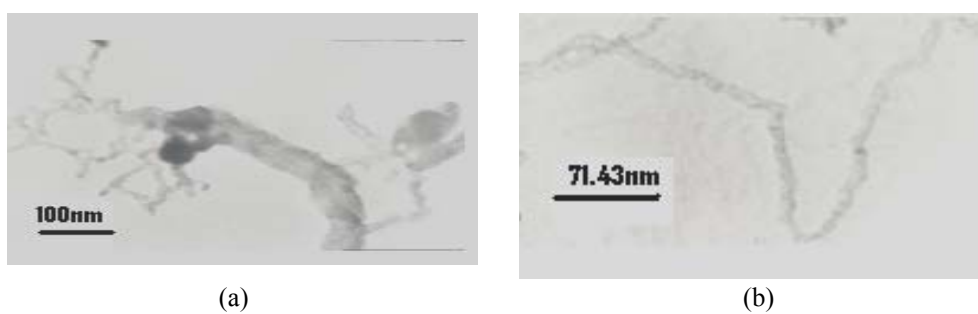


Figure 4. TEM micrographs of carbon from uncatalysed reaction (a) scale 100 nm (b) scale 71.43 nm.

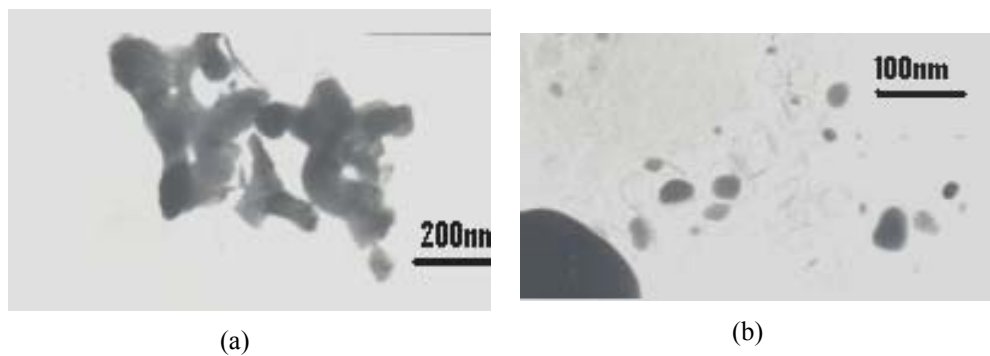


Figure 5. TEM images of Fe particles (a) scale 200 nm (b) scale 100 nm.

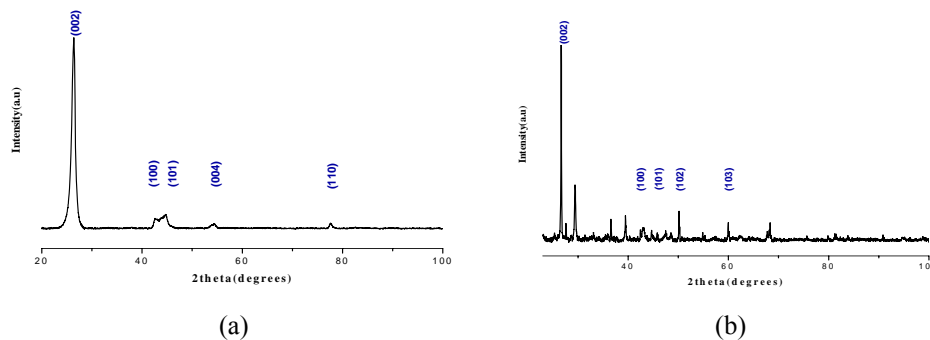


Figure 6. XRD pattern of carbon (a) in presence of Fe nano particle as catalyst (b) without catalyst.

XRD Studies. The X-Ray diffraction (XRD) pattern of the material obtained from catalysed and uncatalysed reactions are presented in Figures 6(a) and 6(b), respectively. The XRD patterns of the samples reveal the characteristics of the graphitized carbon [17-19]. The (002) graphitic lines of the samples were observed at $2\theta = 25.8^\circ$ corresponding to an inter-planar spacing of about 0.343 nm which is usually attributed to CNTs [19]. The patterns also

indicate high degree of crystallinity in case of the catalyzed reaction, which suggests low content of amorphous carbon and impurities by using catalysts of Fe nanoparticles.

4. Conclusions

Carbon nanotubes were obtained by pyrolysis of turpentine oil, an unconventional natural precursor, as a carbon source. The diameters of the CNTs from catalysed reactions was

about 12-15 nm while those from the uncatalysed reactions were about 20-30nm. This research is still ongoing and the preliminary results show that it is promising. The ecologically advantageous and regenerative material may be an effective precursor for the growth of CNTs. This method can be scaled up for mass production.

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