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Waseem Khan[1], Rahul Sharma[2], PK Chaudhury[3], AM Siddiqui[1], Parveen Saini[2]*

[1]Department of Physics, Jamia Millia Islamia, New Delhi-110 025, India
[2]CSIR-National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi-110 012, India
[3]Solid State Physics Laboratory, Timarpur, Delhi- 110 054, India

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***Corresponding author:** Parveen Saini, CSIR-National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi-110 012, India. E-mail: parveensaini580@gmail.com; pksaini@nplindia.org

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Research Article

Synthesis of Carboxylic Functionalized Multi Wall Carbon Nanotubes and Their Application for Static Charge Dissipative Fibers

Abstract

In the present study, multi wall carbon nanotubes (CNTs) were chemically functionalized by concentrated nitric acid refluxing for 8 hours to form acid functionalized CNTs (FCNTs). Fourier transformed infrared spectra reveal the formation of carboxylic acid (-COOH) functional groups on the surface of chemically treated CNTs. The increase in intensity of Raman spectra D band relative to G band and enhancement of oxygen to carbon ratio confirm the functionalization and formation of –COOH groups, which in turn increase the dispersibility of CNTs in water, thus rendering them solution processable. The X-ray diffraction pattern and scanning electron microscopy images confirm the structure retention of CNTs even after harsh acid treatment. These functionalized CNTs show good affinity towards cotton fibers and the surface resistivity of FCNTs coated fiber has been found to be ~ 10^{10} Ω/square making them suitable for use as an anti-static material.

Introduction

The use of electronic gadgets has become widespread and indispensable in the present technological era. This has given birth to an undesirable effect known as electrostatic dissipation (ESD) effect [1] . The accumulation of static charge in electronic goods packaging (which are primarily insulating polymeric materials) causes unnecessary damage to their electronics. Therefore, the importance of development of the ESD free materials has been realized for ultimate utility in electronic packaging. As the electrical conductivity is identified as prerequisite for static charge buildup control, several efforts have been made in the past to develop conducting materials based static safe compositions [2–8]. In particular, CNTs with excellent electrical conductivity, low density, high corrosion resistance, outstanding mechanical properties along with high thermal, chemical and environmental stability [6,9–12] is considered as most promising candidate for ESD control applications. However, their hydrophobicity and the inherent inertness of graphitic skeleton pose major challenges for their direct utilization via formation of CNTs filled composites or surface coatings. To solve these issues CNTs are often modified by covalent and non-covalent schemes (known as functionalization) which enhance their hydrophilicity, processability and compatibility [13–16] . The grafting of oxygen containing functional groups at the open ends and sidewalls of CNTs is a useful approach towards the covalent functionalization of CNTs. Particularly, the carboxylic acid group (i.e. –COOH functionality) happens to be the most common functional groups which open up the possibility of further modification of CNTs via suitable solution based chemical routes. It is worth mentioning that functionalized CNTs contain polar groups which enable their dispersion inside solvents, enhances compatibility with polymeric matrices and improves their ability to surface coat the polymeric substrate based packaging materials [16–20].

Here, we have reported the synthesis of covalently functionalized MWCNTs which can be easily coated over cotton fibers and demonstrated the application of these functionalized CNTs coated fibers for anti- static application.

Experimental

Materials

The MWCNTs used in the experiment was purchased from Nanoshel with diameter 10-20 nm, length 3-8 µm and (>99 %) purity. The 70% nitric acid of analytical grade was procured from Merck Specialties Pvt. Ltd. Cellulose nitrate membrane filters with 0.45 µm pore size produced by Millipore were used in this experiment.

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Functionalization

About 250 mg of pristine MWCNTs was mixed with 200 mL concentrated nitric acid and the mixture was refluxed for 8 hours followed by its ultracentrifugation at 10000 rpm. The FCNT pulp was dispersed in 500 mL distilled water followed by filtration through a cellulose nitrate membrane filter (0.45 µm pore size) using a vacuum filtration assembly. The sample was repeatedly washed with distilled water till neutral pH of filtrate. The filtered FCNTs bedding was dried in a vacuum oven at 80°C for 24h and obtained FCNTs powder was characterized using different techniques. Figure 1a,b, show the schematics of pristine CNTs and functionalized CNTs (FCNTs) respectively whereas Figure 1c shows the actual refluxing setup used to carry out the reaction.

Characterization

The surface morphology was observed using scanning electron microscope (SEM), Model; VT-EVO, MA-10, Carl–Zeiss, UK. Raman data was recorded on Horiba Jobin- Yvon Laser Spectrometer 6400 using 514.5 nm wavelength as excitation source. Fourier transform infrared (FTIR) transmittance data was obtained using Agilent Technologies Cary 630 system using pressed pellets of sample mixed with KBr. The surface resistivity of uncoated and FCNTs coated fiber was measured by surface resistivity meter.

Results and Discussion

FTIR Spectroscopy

Figure 2a shows the FTIR spectra of pristine CNTs and FCNTs where the noticeable peak at ~ 1636 cm^{-1} in both samples corresponds to the stretching vibrations of the carbon-carbon double bonds (i.e. -C=C- bond stretch) which constitute the CNTs backbone. The presence of this peak in both the samples shows that the basic skeleton of CNTs is preserved even after the acid treatment. However, the appearance of additional peak in FCNTs at ~1742 cm^{-1} (-C=O stretch) and reduction in relative intensity of –C=C- stretch peak confirms the successful oxidation and introduction of carboxylic acid (i.e. -COOH) groups over CNTs backbone. These results are complimented by the Raman spectra (Figure 2b which shows that the intensity of D-band relative to G-band (i.e. I_D/I_G ratio) is significantly higher for FCNTs as compared to pristine CNTs. This indicates that a sufficiently large number of defects have been created upon functionalization which can serve as functional handle and active surface sites for the dispersion of CNTs (Figure 2c) inside polar solvents (e.g. water in present case) & their interaction with other species. Further, the absence of any new band and only minor shift in the position of Raman bands (Figure 2b) and XRD peaks (Figure 2d) revealed that the basic structure of CNTs remained unaffected by functionalization.

Field emission scanning electron microscopy (FESEM) & EDX

In harmony with earlier observations, the FESEM images of pristine CNTs (Figure 3a) and FCNTs (Figure 3b) provides the visual evidence of the preservation of structural features of CNTs in FCNTs even after encountering harsh acid treatment conditions.

Figure 3c,d show the EDX spectra of pristine CNTs and FCNTs respectively whereas corresponding inset shows their elemental composition. It is observed that the proportion of carbon and oxygen atoms (i.e. C/O ratio) decreases upon functionalization, which supports the formation of oxygen containing functional groups over CNTs' surface. Interestingly, the attachment of -COOH groups makes the surface of CNTs hydrophilic which not only facilitates their dispersion in water (Figure 2d) but also allows adsorption over suitable substrates. As the CNTs are electrically conducting, their coating over insulating substrates is expected to reduce surface resistivity, which is considered an index to assess the suitability of a material for anti-static application [8,21,22].

Figure 4a,b show the optical images of bare and FCNTs coated fiber respectively. It can be seen that the bare fiber is white in color whereas upon FCNTs coating, the fiber becomes blackish in color due to decoration of adsorbed FCNTs. The coated FCNTs networks are expected to improve the surface conductivity and hence charge dissipation characteristics. Indeed, the surface resistivity measurements have shown that bare cotton fiber is insulating in nature with resistivity

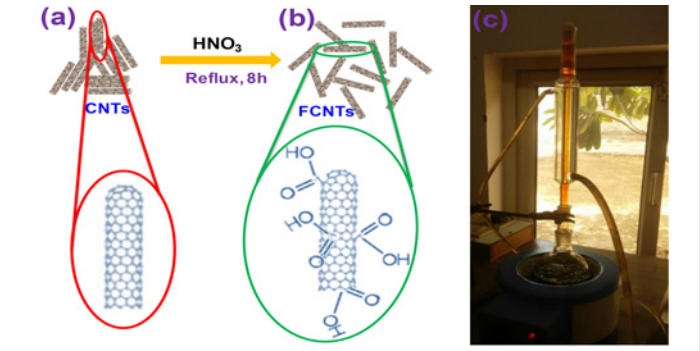

Figure 1: Schematic representation of (a) Pristine CNTs (b) functionalized CNTs (FCNTs); and (c) actual refluxing setup.

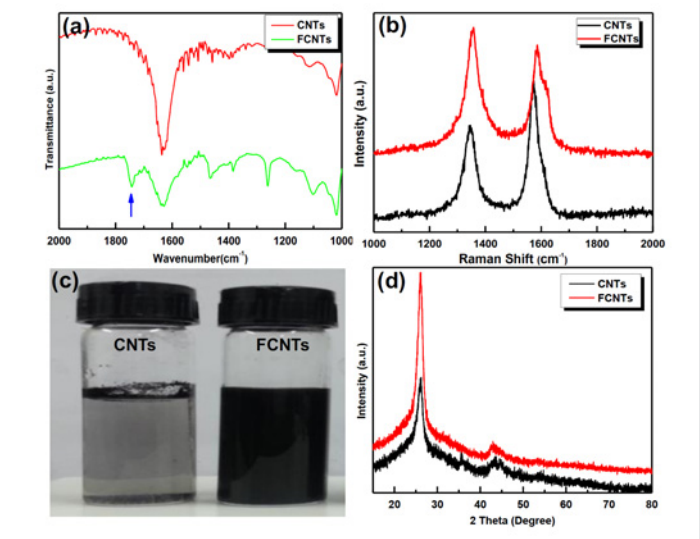

Figure 2: (a) FTIR spectra (b) Raman spectra (c) Dispersion images and (d) XRD Spectra of CNTs and FCNTs.

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value of >10^{12} Ω/square (Figure 4c). In contrast, FCNTs coated fiber displays several orders lower resistivity i.e. 10^{10} Ω/square (Figure 4d) and clearly passes the anti-static criteria [6,23,24]. These fibers are considered potential candidate for making woven fabrics with antistatic & static charge dissipation characteristics, with ultimate utility in ESD safe electronic packaging applications.

Conclusion

The successful functionalization of MWCNTs was achieved in just 8 hours of refluxing in HNO_3. The COOH group was successfully attached on CNTs which is confirmed by the appearance of corresponding peak in its FTIR spectrum. Raman spectroscopy further validates this by exhibiting an increase in D band intensity. The acid treatment is able to functionalize the CNTs without deteriorating their structure which is backed by FESEM images and XRD and patterns. The improved dispersion results as a consequence of functionalization. FCNTs also prove their worth as a possible anti-static material as their surface coating on insulating polymeric fiber brings its resistivity down to ~10^{10} Ω/square.

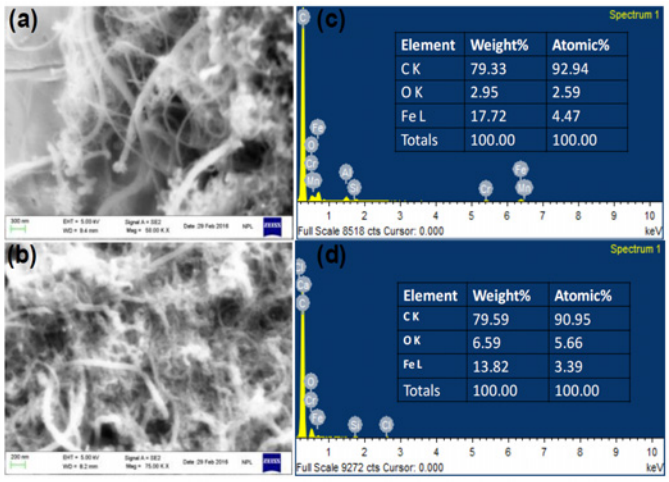

Figure 3: FESEM micrographs of (a) pristine CNTs & (b) FCNTs; and EDX spectra of (c) pristine CNTs & (d) FCNTs.

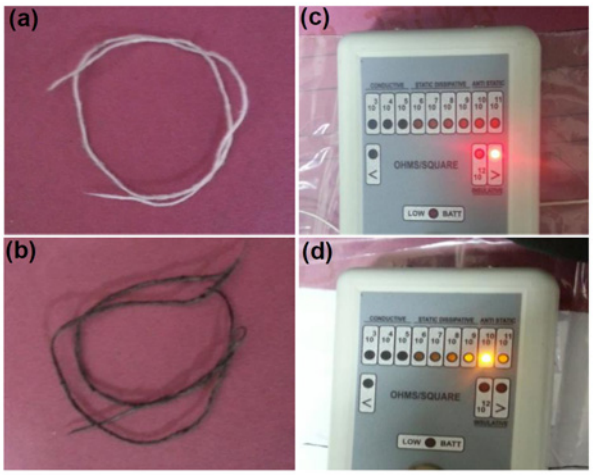

Figure 4: Optical image of (a) bare fiber & (b) FCNTs coated fiber; and surface resistivity of (c) bare fiber & (d) FCNTs coated fiber.

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References

1. Saini P (2015) Intrinsically conducting polymer-based blends and composites for electromagnetic interference shielding: theoretical and experimental aspects. In Fundamentals of Conjugated Polymer Blends, Copolymers and Composites. Edited by Saini P, John Wiley & Sons Inc 449–518. Link: https://goo.gl/B0EoCK

2. Rosner RB (2001) Conductive materials for ESD applications: an overview. IEEE Trans. Device Mater. Reliab 1: 9–16. Link: https://goo.gl/kqFT4M

3. Narkis M, Lidor G, Vaxman A, Zuri L (1999) New injection moldable electrostatic dissipative (ESD) composites based on very low carbon black loadings. J Electrost 47: 201–214. Link: https://goo.gl/WaMoac

4. Soto-Oviedo MA, Araújo OA, Faez R, Rezende MC, De Paoli MA (2006) Antistatic coating and electromagnetic shielding properties of a hybrid material based on polyaniline/organoclay nanocomposite and EPDM rubber. Synth Met 156: 1249–1255. Link: https://goo.gl/svZNYi

5. Li Y, Wang X (2013) Intrinsically conducting polymers and their composites for anticorrosion and antistatic applications. In Semiconducting Polymer Composites. Edited by Yang X, Wiley-VCH Verlag GmbH & Co. KGaA. 269-298. Link: https://goo.gl/oM3Y6E

6. Saini P, Choudhary V (2013) Enhanced electromagnetic interference shielding effectiveness of polyaniline functionalized carbon nanotubes filled polystyrene composites. J Nanoparticle Res 15: 1415. Link: https://goo.gl/xyvKvM

7. Saini P, Sharma R, Akodia S (2016) Graphene oxide and reduced graphene oxide coated polyamide fabrics for antistatic and electrostatic charge dissipation. World J Text Eng Technol 2: 1–5. Link: https://goo.gl/AVLc9z

8. Saini P (2015) Fundamentals of Conjugated Polymer Blends, Copolymers and Composites: Synthesis, Properties and Applications. John Wiley & Sons, Inc. Link: https://goo.gl/HtZAm1

9. Saini P, Arora M (2012) Microwave absorption and EMI shielding behavior of nanocomposites based on intrinsically conducting polymers, graphene and carbon nanotubes. In New Polymers for Special Applications. Edited by De Souza Gomes A InTech. Link: https://goo.gl/uBtLKD

10. Yu M (2000) Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. Science 287: 637–640. Link: https://goo.gl/A1av8f

11. Pop E, Mann D, Wang Q, Goodson K, Dai H (2006) Thermal conductance of an individual single-wall carbon nanotube above room temperature. Nano Lett. 6: 96–100. Link: https://goo.gl/rpz9Nb

12. Charlier JC, Blase X, Roche S (2007) Electronic and transport properties of nanotubes. Rev. Mod. Phys. 79: 677–732. Link: https://goo.gl/IgWakw

13. Chen J, Hamon MA, Hu H, Chen Y, Rao AM, et al. (1998) Solution properties of single-walled carbon nanotubes. Science 282: 95–98. Link: https://goo.gl/LnU1EA

14. Bianco A, Kostarelos K, Partidos CD, Prato M (2005) Biomedical applications of functionalised carbon nanotubes. Chem Commun 571-577. Link: https://goo.gl/S7Xgz4

15. Harrison BS, Atala A (2007) Carbon nanotube applications for tissue engineering. Biomaterials 28: 344–353. Link: https://goo.gl/hSYeq

Citation: Khan W, Sharma R, Chaudhury PK, Siddiqui AM, Saini P (2016) Synthesis of Carboxylic Functionalized Multi Wall Carbon Nanotubes and Their Application for Static Charge Dissipative Fibers. Int J Nanomater Nanotechnol Nanomed 2(1): 025-028. DOI: 10.17352/2455-3492.000011

16. Khan W, Sharma R, Saini P (2016) Carbon nanotube-based polymer composites: synthesis, properties and applications. In Carbon Nanotubes - Current Progress of their Polymer Composites. Edited by Berber MR, Hafez IH InTech, 2016. Link: https://goo.gl/6TxdVv

17. Saini P (2013) Electrical properties and electromagnetic interference shielding response of electrically conducting thermosetting nanocomposites. In Thermoset Nanocomposites. Edited by Mittal V Wiley-VCH Verlag GmbH & Co. KGaA, 2013. 211-237. Link: https://goo.gl/Fc4rLB

18. Song YS, Youn JR (2005) Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites. Carbon 43: 1378–1385. Link: https://goo.gl/IECqtQ

19. O'Connell MJ, Boul P, Ericson LM, Huffman C, Wang Y, et al. (2001) Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping. Chem Phys Lett 342: 265–271. Link: https://goo.gl/xBx2Jd

20. Lau K, Lu M, Cheung H, Sheng F, Li H (2005) Thermal and mechanical properties of single-walled carbon nanotube bundle-reinforced epoxy nanocomposites: the role of solvent for nanotube dispersion. Compos. Sci. Technol. 65: 719–725. Link: https://goo.gl/4alpB8

21. Chubb JN (2007) A Standard proposed for assessing the electrostatic suitability of materials. J Electrost 65: 607–610. Link: https://goo.gl/BFQj8A

22. Saini P, Choudhary V (2013) Electrostatic charge dissipation and electromagnetic interference shielding response of polyaniline based conducting fabrics. Ind J Pure Appl Phys 5: 112–117. Link: https://goo.gl/GRdbxm

23. Saini P, Choudhary V, Singh BP, Mathur RB, Dhawan SK (2011) Enhanced microwave absorption behavior of polyaniline-CNT/polystyrene blend in 12.4–18.0 GHz range. Synth Met 161: 1522–1526. Link: https://goo.gl/PyrHYi

24. Saini P, Choudhary V, Vijayan N, Kotnala RK (2012) Improved electromagnetic interference shielding response of poly(aniline)-coated fabrics containing dielectric and magnetic nanoparticles. J Phys Chem C 116: 13403–13412. Link: https://goo.gl/73SALX

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