Materials Today: Proceedings xxx (xxxx) xxx

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Chemical functionalization of few walled carbon nanotubes produced by chemical vapour deposition technique

T.N. Suresh, T. Somanathan *

Department of Chemistry, School of Basic Sciences, VISTAS, Chennai 600117, India

ARTICLE INFO

Article history:
Received 4 January 2021
Received in revised form 22 February 2021
Accepted 26 February 2021
Available online xxxx

Keywords:
Chemical functionalization
FWCNTs
Catalytic processes
Materials Science
CVD
TEM

ABSTRACT

Materials with well-defined structures in the nanometer scale exhibit unique mechanical, optical and magnetic properties due to size related effects. Among the various nanomaterials studied, carbon nanotubes (CNTs) have great interest in several applications. The field of nanoscience and technology is an interdisciplinary field drawing researchers across materials science, technology and engineering disciplines each trying to exploit the advantages of this emerging field. The functionalized carbon nanotubes by acid-treatment were to afford dispensability in aqueous solution. The oxidized functional carboxyl groups which links the protein either covalently or non-covalently to the nanotubes sidewalls. Chemically functionalized few walled carbon nanotubes (FWCNTs) have promising effect in drug target and exhibit biocompatibility, excretion and less toxicity. CNTs were synthesised by chemical vapour deposition (CVD) method were FeMoMgO used as catalytic template. The purified CNTs were functionalised and it was characterised by FT-IR, SEM, HRTEM and Raman spectroscopy.

Selection and peer-review under responsibility of the scientific committee of the International Conference on Materials, Manufacturing and Mechanical Engineering for Sustainable Developments-2020.

1. Introduction

Carbon nanotubes (CNTs) is one of the promising field in nanotechnology and nanoscience because of its unique properties [1]. Functionalized or modified CNTs utilized effectively as a potential component in nanoscale electronics and nano sensors. The chemical modification on the surface of the nanotubes which may offer a huge chances for reforming the structural and electronic properties. Chemically modified CNTs can able to be fixed by utilizing chemical bonds from the surface of the carbon nanotubes. Functionalized CNTs coupled with organic molecules like dyes, proteins, nucleic acids which may employed in sensor applications [2].

Due to its structural properties CNTs have been used as effective adsorbents for numerous organic pollutants and metal ions. The vision of these applications which primes to functionalization of multi walled carbon nanotubes (MWNTs) [3].

In diverse methods of nanotube production such as like electric arc-discharge [4], laser ablation [5] and catalytic chemical vapor deposition (CCVD) [6], the catalytic method looks to be the effective and promising for bulky industrial applications [7]. The acid treatment are typically removes impurities present in the synthesized samples but it can damage the length of the nanotubes [8]. The oxidation studies clearly indicates that the tips of the nanotubes are much more responsive than the surface [9]. This outcome is obviously indicates because of the slower in the oxidation by strong acids. In this method several functional groups are formed on the surface of the CNTs [10]. These addition of these functional groups on the surface of CNTs improves and modifies the wetting characteristics and enhance the properties of CNTs [11].

Currently, we focused on the efficiency of acid treatments on surface morphology and features of few walled CNTs. The resulting materials of the CNTs were characterized using FT-IR, TEM and Raman spectroscopy.

2. Experimental details

2.1. Synthesis of carbon nanotubes

CNTs samples utilized in this study were produced by catalytic CVD method using FeMoMgO catalyst [12]. For removal of the

* Corresponding author.
E-mail address: soma.sbs@velsuniv.ac.in (T. Somanathan).

https://doi.org/10.1016/j.matpr.2021.02.755
2214-7853/
Selection and peer-review under responsibility of the scientific committee of the International Conference on Materials, Manufacturing and Mechanical Engineering for Sustainable Developments-2020.

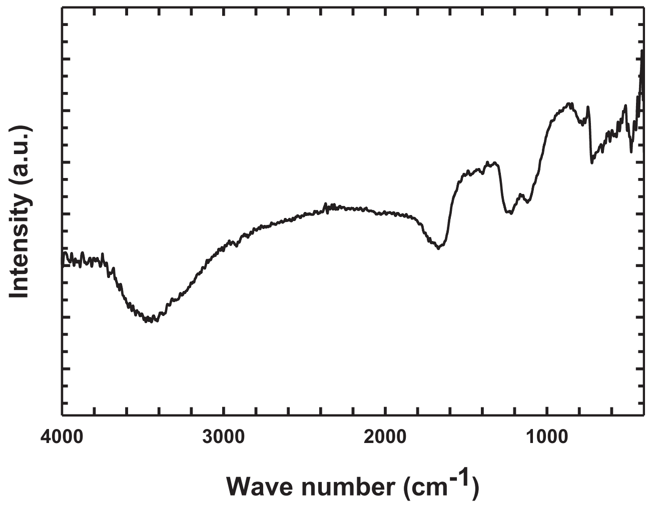

Fig. 1. FT-IR spectrum of functionalized (*f*) few walled CNTs.

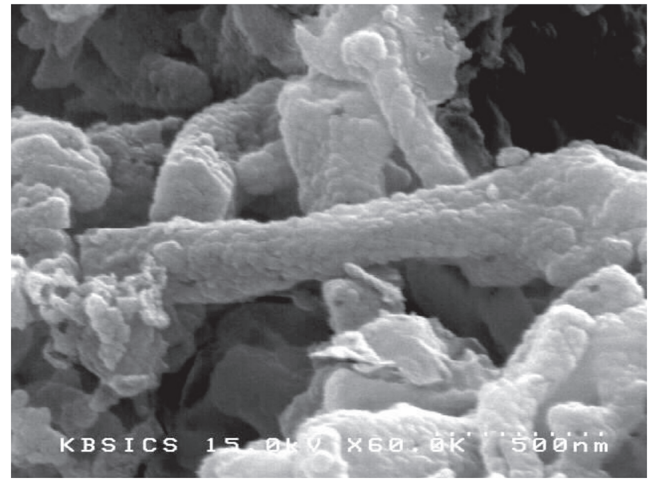

Fig. 2. SEM image of *f-CNTs* after mixture of acids treatment.

support and catalytic particles present in the synthesised materials was treated with 5% nitric acid at ambient temperature.

2.2. Functionalization of nitric acid (NCNTs)

The synthesized CNTs were boiled with 25% nitric acid at 120 °C for 180 min and then the resultant solution was pass through filter, washed and heated at 120 °C in a hot air oven.

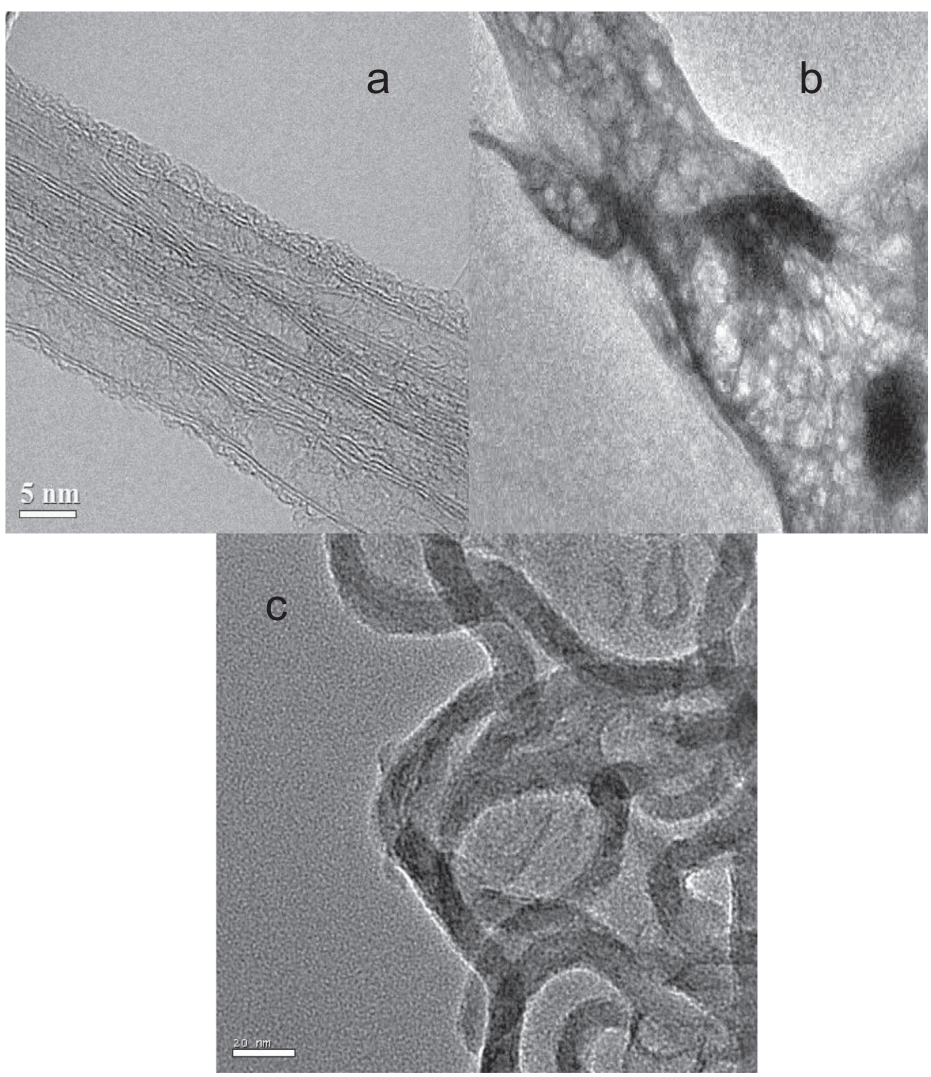

Fig. 3. (a) Few walled CNTs, (b) polymer like structure of FWCNTs and (c) amorphous structure of FWCNTs.

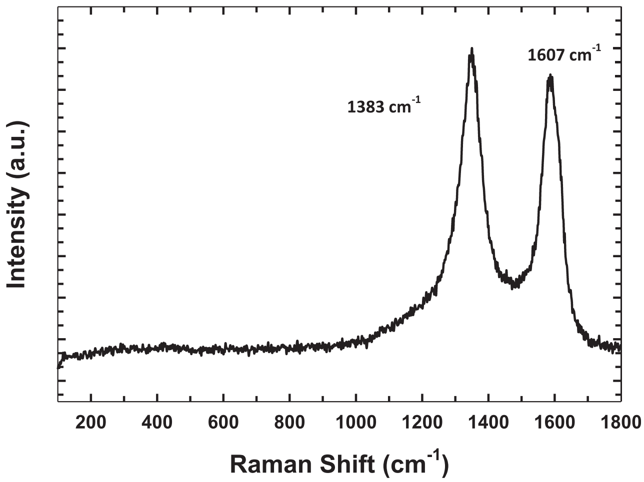

Fig. 4. Raman spectra of functionalized few walled *CNTs* after mixture of acids treatment.

2.3. Functionalization of nitric acid/ sulphuric acid (NSCNTs)

After the removal of silica phase from the synthesised CNTs samples, then it was boiled in a mixture of 3:1 sulphuric acid : nitric acid for 3–4 hr. The final solution was filtered, washed and heated at 120 °C in a hot air oven.

3. Results and discussion

3.1. FT-IR analysis for acid treated CNTs

IR has been widely used in the structural determination of CNTs and its interaction with other molecules. The wide-ranging of peaks between 3395 and 3455 cm^{-1} signifying the presence of –OH groups on the surface of the materials. The peak at 1500–1650 cm^{-1} remain the CO widening mode on the surface of the FWCNTs. The two peaks at 2920 and 2854 cm^{-1} resemble to the C–H stretching. Fig. 1 which indicate that the surface of CNTs were functionalized by carboxylic group.

3.2. Influence of acid treatments in CNTs

The influence of the CNTs with H_2SO_4 opened the surface and broken the tubes at imperfections, giving rise to shorter nanotubes. Acidic oxidation treatment not only breaks CNTs, but also introduces a large number of functional groups on the nanotubes [13]. After being treated with HNO_3 and HNO_3/H_2SO_4 (1:3) CNTs were open ended and separated with relatively shorter length. It illustrates that the oxidation process is successful [14,15].

3.3. SEM and TEM image of f-FWCNTS

Fig. 2 illustrate the scanning electron microscope image of the acid functionalized carbon nanotubes. The FWCNTs product treated with the mixture of H_2SO_4 and HNO_3 show a considerable structural alteration. The structure of FWCNTs was altered into a polymeric materials which clearly shown in Fig. 3. The HRTEM image demonstrations that the FWCNT which reduce the size of the tube which seem to be the shapeless materials which is shown in Fig. 3. These formless CNTs are believed to be reacted products of mixture of FWCNTs [16].

3.4. Raman spectroscopy

Raman spectra of modified FWCNTs are displayed in Fig. 4. The Raman spectrum shows, the peak at

1383 cm^{-1} which representing a more disordered structure and is labeled as the D (disordered) band. The G (graphitic) band reveals the hexagonal lattice of graphite leads to a sharp vibration mode at 1607 cm^{-1}, which is due to presence of C sp^2 domains. From these results, we showed a modification of FWCNTs diameter by oxidation of CNTs by acid treatment was observed in Raman Spectrum.

4. Conclusion

Carbon nanotubes are among the novel emerging technologies with potential application to drug, vaccine and gene delivery systems. Carboxylic (–COOH) were effectively functionalized on the surface of the CNTs. The oxidization improved the specific surface area and enhanced the characteristic structure of the CNTs. From the TEM results we confirm that the metal particles used for the synthesis of CNTs were purified by acid treatment. Surface alteration of FWCNTs by oxidation was observed in FT-IR spectroscopy. Finally, we presented that FWCNTs morphology able to significantly adjust by a mixed acid treatment.

Declaration of Competing Interest

There is no declaration of competing interest

Acknowledgements

The authors are grateful to Central Instrumentation Laboratory (CIL) VISTAS, Chennai for the providing infrastructure facilities.

References

[1] P.M. Ajayan, Chem. Rev. 99 (1999) 1787–1800.
[2] U.D. Welikowska, J.M. Benoit, P.W. Chu, R. Graupner, S. Lebedkin, S. Roth, Curr. Appl. Phys. 2 (2002) 497–501.
[3] Y. Wang, Z. Iqbal, S.V. Malhotra, Chem. Phys. Lett. 402 (2005) 96–101.
[4] D.S. Bethune, C.H. Kiang, M.S. deVries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Nature 363 (1993) 605–607.
[5] T. Guo, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, Chem. Phys. Lett. 243 (1995) 49–54.
[6] V. Ivanov, A. Fonseca, J.B. Nagy, A. Lucas, P. Lambin, D. Bernaerts, X.B. Zhang, Carbon 33 (1995) 1727–1738.
[7] J. Geng, G. Singh, D.S. Shephard, M.S.P. Shaffer, B.F.G. Johnson, A.H. Windle, Chem. Commun. (2002) 2666–2667.
[8] N. Zhang, J. Xie, V.K. Varadhan, Smart, Mater. Struct. 11 (2002) 962.
[9] S. Nagasawa, M. Yudasaka, K. Hirahara, T. Ichihashi, S. Iijima, Chem. Phys. Lett. 328 (2000) 374–380.
[10] H.T. Gomes, P.V. Samant, P. Serp, P. Kalck, J.L. Figueiredo, J.L. Faria, Appl. Catal. B 54 (2004) 175–182.
[11] J. Garcia, H.T. Gomes, P.V. Samant, P. Serp, P. Kalck, J.L. Figueiredo, J.L. Faria, Catal. Today 102–103 (2004) 101.
[12] T. Somanathan, A. Pandurangan, New Carbon Materials 25 (2010) 175–180.
[13] W. Jian, D. Lau, Composite Sci. Tech. 191 (2020) 108076.
[14] G.X. Tham, A.C. Fisher, R.D. Webster, Electrochimica Acta. 357 (2020) 136880.
[15] F. Rodriguez-Reinoso, Carbon 36 (1998) 159–175.
[16] A.G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C.B. Huffman, F.J. Rodriguez- Macias, P.J. Boul, A.H. Lu, D. Heymann, D.T. Colbert, R.S. Lee, J.E. Fischer, A.M. Rao, P.C. Eklund, R.E. Smalley, Appl., Phys. A 67 (1998) 29–37.