The Growth of Carbon Nanotubes via Chemical Vapor Deposition Method; its Purification and Functionalization

Beant Kaur Billing¹*, Narinder Singh² and Prabhat K. Agnihotri¹

¹School of Mechanical, Materials and Energy Engineering, Indian Institute of Technology, Ropar – 140001, Punjab, India; beant.kaur@iitrpr.ac.in
²Department of Chemistry, Indian Institute of Technology, Ropar – 140001, Punjab, India

Abstract

Objectives: The main motive behind proposed work is to enhance the solubility of CNTs in aqueous medium and in various other solvents. Purification and functionalization helped in accomplishing aforementioned task. Methods/Statistical Analysis: Initially, CNTs were grown by Chemical Vapor Deposition method. Nickel metal catalyst solution was prepared and loaded onto SiO₂ wafer, which is kept in vacuum assisted quartz tube. Acetylene was used as a hydrocarbon source and at 750 °C it decomposes at nickel metal surface resulting in growth of Carbon Nanotubes. Several characterizations such as SEM, EDX, XRD and FTIR were performed for confirmation of CVD grown CNTs. SEM confirms the formation of tubular structure i.e. carbon nanotube and EDX illustrates the presence of carbon and metal catalytic impurities. Findings: Such impurities restrict their use in physical, chemical, biological and environmental systems, thus purification is required. Among all purification methods, acid treatment suits best for removal of metallic impurities. An acid mixture of H₂SO₄ and HNO₃ in ratio of 3:1 was utilized to remove the impurities present. These acid purified CNTs now contain carboxylic acid groups attached over defects, sidewalls and at ends. However another major shortcoming of CNTs is their insolubility in various liquids and polymers. Improvements: Therefore, to improve the solubility and to allow bonding with polymer matrix, amide functionalization was carried out. By the effect of thionyl chloride, the -OH bond was replaced by –Cl group, which was further replaced by -NH moiety. Characterizations were carried out at each step of CNT processing. Moreover, these functionalized CNTs encourages us to extend the present work to quantify the effect of as grown and f-CNT on the average static and dynamic mechanical properties of CNT/epoxy nanocomposites in future.

Keywords: Carbon Nanotube, Chemical Vapor Deposition, Functionalization, Growth, Purification

1. Introduction

Carbon Nanotubes (CNTs) are one of the most exciting and widely used nanomaterials since its discovery. Carbon nanotube is an allotrope of carbon, present in sp²-hybridized form. It is cylindrical in nature, having a very high aspect ratio. CNTs can be conducting, semi-conducting and insulating depending upon its geometry. If n=m, it is said to be metallic; if n−m=3j, it is said to...
be insulating; else semiconductors where n and m are chiral indices of CNT.\textsuperscript{1} It offers unique physical, chemical and electronic properties due to its distinct structure.\textsuperscript{4} CNTs are stronger than steel, harder than diamond, more electrical conductive than copper, offer high thermal conductivity than diamond and many more.\textsuperscript{2} Hence CNTs offer many applications in different fields of nanotechnology. Consequently CNTs has become a material of common interest today. Various synthetic approaches such as arc discharge, laser ablation and low-pressure flame were developed aiming at producing CNTs.\textsuperscript{2} But due to the high degree control and scalability of Chemical Vapor Deposition (CVD) technique, it has become a standard mode of producing comparatively pure CNTs. It also offers low setup cost, high production yield and ease of scale-up.\textsuperscript{2} Therefore, CVD is the best method to grow CNTs; it requires metal catalyst nanoparticles on a support material such as SiO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3} wafer.\textsuperscript{3} Transition metals are well chosen because it offers high solubility of carbon atoms at high temperature and provides strong adhesion.\textsuperscript{2} Catalyst deposition can be manual or by using physical vapor deposition, sputtering, thermal evaporation etc.\textsuperscript{14} Catalyst deposited on the substrate was heated to a temperature of 600-1000°C and exposed to the hydrocarbon source flowing through the quartz tube. Hydrocarbon gas dissociates at the catalyst surface and carbon precipitation results in growth of nanotubes.\textsuperscript{11} The CVD growth technique is versatile in the sense of harnessing plenty of hydrocarbons in any state (solid, liquid or gas) which enables the use of different substrates, and allows CNT growth in variety of forms, such as powder, film, aligned or entangled, straight or coiled nanotubes or any chosen architecture of nanotubes on predefined sites of a patterned substrate.\textsuperscript{11} Therefore, we can say, CVD offers better control on growth parameters. The physical characteristics of CNTs depend upon the dimensions of catalyst used and growth conditions in a CVD process. Resulting carbon nanotubes can follow tip growth or base growth mechanism. There are two general cases of CNT growth. In the first case, when the interactions between catalyst and substrate are weak, hydrocarbon decomposed at top of metal surface, carbon particles diffuse down through the metal and the CNT precipitates across the metal bottom, it pushes the whole metal particle off the substrate and CNT continues to grow in vertical direction. Once the metal is fully covered with excess carbon, its catalytic activity terminates and the CNT growth is stopped. This is known as a tip-growth model. In other case, when the interaction between catalyst and substrate is strong, CNT precipitation fails to push the metal particles up and the hydrocarbon decomposition takes place on the lower peripheral surface of the metal. Thus CNT grows up with the catalyst particle rooted on its base and this is known as base-growth model.\textsuperscript{13} But the CVD method is still lagging behind in terms of 100% purity of CNTs because it contains residual metal catalyst as impurity and some amount of carbon impurity along with CNTs.\textsuperscript{14} To improve the purity of CNTs produced, some chemical and physical methods have been developed. Chemical methods include treatment with acid, base or both because metal impurities get dissolved in acid and can be filtered out. Physical method includes physical separation on the basis of physical appearance, aspect ratio, magnetic properties, etc.\textsuperscript{15} However, the physical method is comparatively less effective and time consuming as compared to chemical one. Acid treatment offers high purity of CNTs and leads to carboxylic acid (-COOH) group attachment on sidewalls, ends and at defects of CNTs.\textsuperscript{14} It increases solubility of CNTs in various liquids, polymers and solvents, which was restricted in case of grown CNTs. It offers binding sites to further functionalize the CNT with amine, amide, aldehydes etc. Such functionalization methods may lead to offer applications in different fields of drug delivery, sensing, water purification and various biomedical processes.\textsuperscript{12}

This work is focused on growth of CNT by thermal CVD method using nickel as a catalyst. The motivation of current work is to develop a simple strategy of amine
functionalized CNTs in order to use it for diverse applications. Scanning Electron Microscopy (SEM) and Energy dispersive X-ray (EDX) generalized morphology and composition of CNTs, whereas functional group attachment was verified by FTIR. XRD characterization was also performed to check crystalline nature as well as diameter of CNTs.

2. Experimental

2.1 Material and Methods
All chemicals used were of analytical reagent grade and purchased from Sigma-Aldrich and used as received without further purification. All studies were carried out in de-ionized water obtained from Millipore Millisystem having resistivity not less than 18 MΩcm. A substrate material SiO$_2$ wafer used for CNT growth was bought from Macwin India, which was oxidized at 700°C and having oxide layer thickness as 200nm. CNTs were grown on Thermal Chemical Vapour Deposition system of Technos instruments which runs in single phase at frequency of 50 Hz and power of 10kVA. Morphology of CNTs was checked on Scanning Electron Microscope using SEM JEOL JSM-6610-LV at voltage of 10kV. EDX analysis was performed on Inca instrument constituted with SEM to check the elemental composition. X-Ray Diffraction (XRD) patterns were recorded in the 2θ range of 5–80° with a scan speed of 2°/min on a PANalytical X’PERT PRO diffractometer using Cu Kα radiation ($\lambda=0.1542$ nm, 40 kV, 20 mA). Fourier Transform Infra Red spectrum was recorded on Bruker spectrophotometer in the range of 600-3800 cm$^{-1}$ (spectral resolution= 4 cm$^{-1}$; number of scans = 100).

2.2 Selection of Catalyst
For synthesizing CNTs, typically, metal nanoparticles are requisite to enable hydrocarbon decomposition. Most commonly used metals are Fe, Co, Ni, because of two main reasons: (i) high solubility of carbon in these metals at high temperatures; and (ii) high carbon diffusion rate in these metals. Besides that, high melting point and low equilibrium-vapor pressure of these metals offer a wide temperature window of CVD for a wide range of carbon precursors. Literature also states that solid organometal-locenes (ferrocene, cobaltocene, nickelocene) are also widely used as a CNT catalyst. Apart from the popular transition metals (Fe, Co, Ni), other metals of this group, such as Cu, Au, Ag, Pt, Pd were also found to catalyze various hydrocarbons for CNT growth. On the role of CNT catalysts, it is worth mentioning that transition metals are proven to be efficient catalysts. Therefore, we prefer transition metal nanoparticles to provide surface for hydrocarbon decomposition. It is a general experience that the catalyst-particle size dictates the tube diameter. Hence, metal nanoparticles of controlled size, pre-synthesized by reliable techniques, can be used to grow CNTs of controlled diameter. Thin films of catalyst coated on various substrates are also proven good in getting uniform CNT deposits. The key factor to get pure CNTs is achieving hydrocarbon decomposition on the catalyst surface.

In a typical procedure, a silicon wafer originally oxidized at 700°C for 2 hours was used as a substrate. Nickel (Ni) metal catalyst was employed to provide better nucleation sites for the growth of CNTs. For this purpose a catalyst solution was prepared by adding different nickel constituents such as Nickel Sulphamate as the main source of nickel, Nickel Chloride as an activating agent, Boric acid as a pH buffer, Do-decyl Sodium Sulfate as anti pitting additive and Sodium Saccharin as a primary brightener were dissolved in deionized water and heated up to 55°C temperature. Table 1 provides information about the concentration of all the constituents added in de-ionized water.
2.3 CNT Catalyst Support

As we know, same catalyst works differently on different support materials. Commonly used substrates in CVD are graphite, quartz, silicon, silicon carbide, silica, alumina, alumino-silicate, CaCO$_3$, magnesium oxide, etc. For an efficient CNT growth, the interaction between catalyst and substrate should be investigated with utmost attention. The substrate material, its surface morphology and textural properties greatly affect the yield and quality of the resulting CNTs. In this work, a droplet of prepared nickel solution was manually poured on a silicon wafer and dried for some time before exposing it to the CVD furnace.

2.4 Growth of CNT

CVD is a simple chemical method to produce good quality of CNTs. A hydrocarbon vapour when comes in contact with the “hot” metal nanoparticles, first decomposes into carbon and hydrogen species; hydrogen flies away and carbon gets dissolved into the metal. After reaching the carbon-solubility limit in the metal at high temperature, as-dissolved carbon precipitates out and crystallizes in the form of a cylindrical network having no dangling bonds and hence energetically stable. Hydrocarbon decomposition (being an exothermic process) releases some heat to the metal’s exposed zone, while carbon crystallization (being an endothermic process) absorbs some heat from the metal’s precipitation zone. This precise thermal gradient inside the metal particle keeps the process on. Briefly, a nickel catalyst loaded SiO$_2$ wafer in alumina boat was kept in quartz tube. Here the primary stage was vacuum generation in the range of 10$^{-2}$ torr in the quartz tube using a roughing pump. Process of CNT growth was initiated by the formation of inert atmosphere, where Argon gas was being consumed, followed by reduction with hydrogen gas for 10 minutes and then acetylene for 15 minutes which act as a carbon source to grow CNTs.

### Table 1. Composition of nickel catalyst prepared for CNT growth

| Chemical name                  | Purpose                  | Amount     |
|-------------------------------|--------------------------|------------|
| Nickel Sulphamate             | Source of nickel         | 7.806 moles|
| Nickel Chloride               | Activating agent         | 0.218 moles|
| Boric acid                    | pH buffer                | 1.180 moles|
| Do-decyl sodium sulphate      | Anti-pitting additive    | 0.014 moles|
| Sodium saccharin              | Primary brightner         | 0.056 moles|
The growth process of CNT was shown below in Table 2. Acetylene was used at a pressure of 40 torr at tempera-

ture of 750°C having 60sccm flow rate along with Argon. Flowing argon gas supported cooling.

2.5 Purification cum Functionalization with COOH Group

Since the CNT growth mechanism via CVD is based on metal catalyst assisted hydrocarbon decomposition, therefore residual metal impurities and some carbonaceous impurities were found with the grown CNTs. Hence grown CNTs were further processed for purification. It was subjected to chemical treatment for removal of residual metal catalyst and in order to remove the amorphous

Figure 1. Acid treatment for purification of CNTs.
carbon it was processed to thermal treatment. CNTs were mixed in H$_2$SO$_4$ and HNO$_3$ solution in 3:1 ratio as shown in Figure 1. The mixture was first stirred at 0°C, then at room temperature and finally at 70°C for 5 hours each. It was followed by immediate quenching for another 1 hour. Continuous washing was offered to remove free acid from CNTs followed by centrifugation; first by adding ethanol followed by acetone and then water. Cartoonic representation of acid treatment for CNT purification has been shown in Figure 1. This purification results in attachment of COOH group on the surface of CNT, which ensures functionalization with COOH group.

2.6 Functionalization with Amine

COOH functionalized CNTs offers possibility of binding with amine. Reaction initialized by first treating carboxylic group constituting CNTs with thionyl chloride. In round bottom flask, an amount of 100mg CNT was taken and dissolved in 1ml DMF, additionally 15 ml of thionyl chloride was added. Reaction continued at reflux for a few hours at a temperature of 80 °C. After completion of the reaction, thionyl chloride was evaporated and CNTs were dried in an oven. In the next step, dried CNTs were dissolved in hydrazine hydrate to attach the amine group to CNTs, reaction continued at reflux for 3 hours main-

![Figure 2. Schematic representation of CNT functionalization at various steps.](image-url)
3. Results and Discussion

3.1 CNT Growth

CNTs were grown in thermal CVD using nickel catalyst Table 1 following the reaction process mentioned in Table 2. The vacuum pump attached to system was used to create $10^{-2}$ torr vacuum. First of all Argon gas has been drawn into the quartz tube to develop an inert atmosphere, after that hydrogen gas was drawn to etch the substrate surface and then acetylene, used as a main source of carbon, which get decomposed on catalyst surface by the effect of heat, results in CNT growth. Formed CNTs were then characterized with SEM, EDX, XRD and FTIR.

3.2 Functionalization of CNT

Functionalization of CNTs is a 3-step process. In order to purify the CVD grown CNTs, it was subjected to treat with acid mixture $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ in 3:1 ratio. During the purification of CNT with acid mixture, $-\text{COOH}$ group gets attached at the side walls, ends and at the defects of CNTs. Carboxylic acid functionalized CNTs were then converted to acid chloride CNTs by treating it with thionyl chloride. During 2nd step of process, an amount of 50mg CNT-COOH was taken and dissolved in DMF and thionyl chloride. Reaction continued for a few hours at reflux keeping 80°C temperature. Resulting CNTs were filtered and dried in oven. In 3rd step, CNTs were reacted with hydrazine hydrate for 3 hours at reflux maintaining 100°C temperature. Here the amine group reacts with acid chloride group, resulting in attachment of amide linkage at CNT surface. Attachment of a long hydrocarbon chain improves solubility of CNT. Prepared samples were fully characterized with SEM, EDX, XRD and FTIR.

3.3 Characterization

CNTs grown and functionalized at various step were characterized using SEM, EDX, XRD and FTIR techniques discussed further. Different micrographs have been obtained in the micron range to check morphology of CNTs before and after treatment with carboxylic acid. Figure 3a shows a bundle of CNTs prepared from CVD, without any purification. It is quite clear that impurities are also present along with grown CNTs. EDX analysis has also been performed, which shows the presence of metal catalyst as impurities. Nickel, sodium, sulphur and phosphate elements were found along with carbon in Figure 4a. CVD prepared CNTs were then treated with a carboxylic acid mixture that removes impurities from CNTs. It can be analyzed from SEM micrographs post acid treatment that CNTs are found to be pure as shown in Figure 3b. Amine functionalized CNTs were also captured by SEM and are shown in Figure 3c. EDX spectrum shows the presence of only carbon and oxygen, which declares acid treatment, has removed the metal catalyst impurity. Figure 4b shows elemental composition of purified CNTs. The amorphous carbon present in the product was removed by oxidizing the CNTs in a muffle furnace at 400°C for 2 h. Further Figure 4c showed the presence of nitrogen, which depicts amine functionalization of CNTs. XRD characterization illustrated in Figure 5 has also been performed before and after purification. It can be observed from XRD graphs that after purification XRD peaks are quite sharp which shows improved crystallinity of CNTs. Hence it was declared from SEM, EDX and XRD characterization that CNTs were purified and further functionalized with different group. Further amine functionalization was verified from FTIR. It gives information about attachment of amine functional group. This completes the functionalization of CNTs. In Figure 6, black line shows the CVD grown CNTs, where C=C
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Figure 3. a) SEM micrograph of a) CVD grown CNTs, b) COOH functionalized CNTs and C) amide functionalized CNTs.
Figure 4. a) EDX spectrum of a) unpurified CNTs, b) COOH functionalized CNTs and amide functionalized CNTs.
Figure 5. XRD spectrum of A) as grown CNTs and B) COOH treated CNTs.

Figure 6. FTIR spectrum of as grown CNTs, COOH treated CNTs and Amide functionalized CNTs.
peak is shown at 1575 cm$^{-1}$. COOH functionalized CNTs is shown by red color, where a new band originated at 1725 cm$^{-1}$ for C=O and a broad OH band obtained at 3400 cm$^{-1}$ along with C=C and =C-OH groups. Further amine functionalized CNTs is shown in blue color, where 1725 cm$^{-1}$ C=O peak merged to O=C-NH-NH$_2$ and slightly shifted to 1428 cm$^{-1}$ but a shoulder is observed at 1600 cm$^{-1}$. Hence, above characterization techniques confirm the growth of Carbon Nanotubes via chemical vapor deposition method.

4. Discussion

By the phenomenon of decomposition of hydrocarbon gas onto the surface of nickel metal catalyst inside a CVD chamber at high temperature, resulted in growth of CNTs. Grown CNTs were successfully purified, functionalized and fully characterized using different techniques. Functionalization has improved quality and solubility of CNTs. It motivates us to extend the amine functionalization to various other groups. Functionalization of CNTs can be explored to diverse range of applications in polymer matrix membrane, sensor, water purification etc.

5. Conclusion

A CVD method has been employed to grow good quality CNTs in a reaction furnace. CNTs were obtained by decomposition of acetylene gas at 750°C temperature. CVD grown CNTs were then processed to purification to remove metallic and amorphous impurities. CNTs were treated with acid mixture for 15 hours at different temperature and resulted in pure CNTs isolated from impurities. Obtained CNTs were then treated with thionyl chloride, which enables amide functionalization easier. Hydrazine hydrate was further added to functionalize acid chloride CNTs with amine group. Hence amine functionalized CNTs were obtained by 3-step reaction. SEM, EDX, XRD and FTIR characterization techniques shed light on the changes occurred in CNTs at every step. It was found that functionalization has enhanced the solubility of CNTs in various solvents.

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7. References

1. Iijima S. Helical microtubules of graphitic carbon. Nature. 1991 Nov; 354:56–8. Crossref.
2. Wang X, Li Q, Xie J, Jin Z, Wang J, Li Y, Jiang K, Fan S. Fabrication of ultra long and electrically uniform single-walled carbon nanotubes on clean substrates. Nano Letters. 2009 Sep; 9(9):3137–41. Crossref. PMid:19650638
3. Wilder JWG, Venema LC, Rinzler AG, Smalley RE, Dekker C. Electronic structure of atomically resolved carbon nanotubes. Nature. 1998 Jan; 391(1):59–62. Crossref.
4. Dresselhaus MS, Dresselhaus G, Jorio A. Unusual properties and structure of carbon nanotubes. Annual Review of Material Research. 2004 Aug; 34:247–78. Crossref.
5(a). Yu MF, Lourie O, Dyer MJ, Moloni K, Kelly TF, Ruoff RS. Strength and breaking mechanism of multi-walled carbon nanotubes under Tensile Load. Science. 2000 Jan; 287:637–40. Crossref. PMid:10649994 5(b). Popov M, Kytotani M, Nemanich R, Koga Y. Superhard phase composed of single-wall carbon nanotubes. Physical Review B. 2002 Jan; 65(3):0334081–4. Crossref.
5(c). Hong S, Myung S. Nanotube Electronics: A flexible approach to mobility. Nature Nanotechnology. 2007 Apr; 2:207–8. Crossref. PMid:18654263
5(d). Thostenson E, Li C, Chou T. Nanocomposites in context. Composites Science and Technology. 2005 Mar; 65:491–516. Crossref.
6(a). Eatermadi A, Daraee H, Karimkhanloo H, Kouhi M, Zarghami N, Akbarzadeh A, Abasi M, Hanifehpour Y, Joo SW. Carbon nanotubes: Properties synthesis purification and medical applications. Nanoscale Research Letters. 2014 Aug; 9(1):393–405. PMid:25170330 PMCID:PMC4141964
6(b). Guo T, Nikolaev P, Thess A, Colbert D, Smalley R. Catalytic growth of single-walled nanotubes by laser vaporization. Chemical Physics Letters. 1995 Jun; 243:49–54. Crossref.
7. Inami N, Mohamed MA, Shikoh E, Fujiwara A. Synthesis-condition dependence of carbon nanotube growth by alcohol catalytic chemical vapor deposition method. Science and Technology of Advanced Materials. 2007 Feb; 8(4):92–5. Crossref.

8(a). Aguiar MR, Verissima C, Ramos AC, Moshkalev SA, Swart JW. Synthesis of Carbon Nanotubes and Nanofibers by thermal CVD on SiO2 and Al2O3 support layers. Journal of Nanoscience and Nanotechnology. 2009 Jul; 9(7):4143–50. Crossref.

8(b). Harutyunyan AR. The catalyst for growing single-walled carbon nanotubes by catalytic chemical vapor deposition method. Journal of Nanoscience and Nanotechnology. 2009 Apr; 9(4):2480–95. Crossref. PMid:19437993

9. Hofmann S, Blume R, Wirth CT, Cantoro M, Sharma R, Ducati C, Havecker M, Zafeiratos S, Schnoerch P, Oesterich A, Teschner D, Albrecht M, Gericke AK, Schlogl R, Robertson J. State of transition metal catalysts during carbon nanotube growth. Journal of Physical Chemistry C. 2009 Jan; 113(5):1648–56. Crossref.

10. Saheed MSM, Mohamed NM, Burhanudin ZA. Effect of different catalyst deposition technique on aligned multiwalled carbon nanotubes grown by thermal chemical vapor deposition. Journal of Nanomaterials. 2014 Apr; 2014:1–11.

11. Jourdain V, Bichara C. Current understanding of the growth of carbon nanotubes in catalytic chemical vapor deposition. Carbon. 2013 Jul; 58:2–39. Crossref.

12. Kumar M, Ando Y. Chemical Vapor deposition of carbon nanotubes: A review on growth mechanism and mass production. Journal of Nanoscience and Nanotechnology. 2010 Jun; 10(6):3739–58. Crossref. PMid:20355365

13. Kumar M. Carbon Nanotube Synthesis and Growth Mechanism. In: Carbon Nanotubes- Synthesis Characterization Applications. Siva Yellampalli (ed.). In: Tech Publ: Croatia; 2011. p. 147–70. Crossref. PMCID:PMC3218229

14. Hou PX, Liu C, Cheng HM. Purification of carbon nanotubes. Carbon. 2008 Dec; 46(15):2003–25. Crossref.

15. Furtado CA, Kim UJ, Gutierrez HR, Pan L, Dickey EC, Eklund PC. Debundling and dissolution of single walled carbon nanotubes in amide solvents. Journal of American Chemical Society. 2004 May; 126(19):6095–105. Crossref. PMid:15137775

16. Datsyuk V, Kalyva M, Papagelis K, Parthenios J, Tasis D, Siokou A, Kallitsis I, Galiotis C. Chemical oxidation of multiwalled carbon nanotubes. Carbon. 2008 Feb; 46(6):833–40. Crossref.

17. Wu HQ, Wei XW, Shao MW, Gu JS. Synthesis of zinc oxide nanorods using carbon nanotubes as templates. Journal of Crystal Growth. 2004 Jan; 265(1-2):184–9. Crossref.

18. Baker RTK, Harris PS, Thomas RB, Waite RJ. Formation of filamentous carbon from iron cobalt and chromium catalyzed decomposition of acetylene. Journal of Catalysis. 1973 Jul; 30(1):86–95. Crossref.

19. Hua Z, Liu Y, Yao G, Wang L, Ma J, Liang L. Preparation and Characterization of Nickel coated carbon Fibers by Electroplating. Journal of Material Engineering and Performance. 2012 Mar; 21(3):324–30. Crossref.

20. Porro S, Musso S, Vinante M, Vanzetti L, Anderl M, Trotta F, Tagliaferro A. Purification of Carbon nanotubes by thermal CVD. Physica E. Low dimensional systems and nanostructures. 2007 Mar; 37(1-2):58–61. Crossref.